

Spectroscopic Studies of Some Substituted Methyl Formates

Part 1.—Microwave Spectra and Internal Rotation Barriers of Methyl-fluoroformate, -propiolate, -cyanoformate, -acrylate and -acetate

BY G. WILLIAMS,* N. L. OWEN AND J. SHERIDAN

Chemistry Department, University College of North Wales, Bangor, Caerns

Received 6th July, 1970

The stable molecular conformations of methyl-fluoroformate, -propiolate, -cyanoformate, -acrylate (cis) and -acetate have been shown to be planar, and for the latter four compounds the cis ester molecular skeleton has been established. Barriers to internal rotation of the methyl group were measured from splittings of the microwave lines for each compound. [XCOOCH_3 ; X = F, $V_3 = 1077$; X = HCC, $V_3 = 1266$; X = CN, $V_3 = 1172$; X = CH_3 , $V_3 = 1215$; X = CH_2CH , $V_3 = 1220$ (values of V_3 in cal/mol).] For methyl acetate a value of 307 ± 50 cal/mol for the acetyl methyl group was calculated from internal rotation splittings in the spectrum of $\text{CD}_3\text{COOCD}_3$. The dipole moments of methyl-fluoroformate and cyanoformate were 2.83 and 4.23 D respectively.

The intramolecular forces affecting hindered internal rotation in molecules are of interest to both experimentalists and theoreticians; such attention from theoreticians is attributable to accurate, experimentally determined data available on barriers to internal rotation. This article reports our findings of a study of such potential barriers for five substances each containing the methoxy ($\text{O}-\text{CH}_3$) group. We have investigated, by microwave spectroscopy, a series of substituted methyl formates with a view to examining the effect of substitution on the stable molecular conformation and on the barrier to internal rotation of the methyl group. A careful study of such a series of homologous molecules should provide an insight into factors that affect the internal rotation. All the compounds studied are carboxylic esters which may conveniently be considered as being derived from methyl formate (HCOOCH_3) by replacement of the formyl hydrogen by other functional groups.

With the exception of methyl acetate, no isotopic species of these compounds were studied, but in view of the fact that the molecular geometry of methyl formate has been studied in detail by Curl,¹ this omission does not seriously detract from our conclusions regarding these compounds. For methyl acetate the presence of two dissimilar methyl tops create special difficulties and it was necessary to study all four possible species of the fully deuterated methyl groups in order to interpret the spectral data. Our analysis of the spectrum of methyl acetate (although only preliminary) represents the first microwave internal rotation study of a molecule with two dissimilar methyl groups.²

EXPERIMENTAL

Rotational spectra were obtained using a conventional 100 kHz Stark modulated microwave spectrometer with an X-band copper cell. Most measurements were carried out with the cell between -70°C and room temperature. Absorption frequencies, which are

* present address: Plastics Division, I.C.I., Welwyn Garden City, Herts.

believed to be accurate to ± 0.05 MHz, were measured using a Schlumberger D0 1001/0 1500 precision signal generator frequency-locked to a Hewlett-Packard 5090A Droitwich receiver.

METHYL FLUOROFORMATE was prepared by the method of Goswami and Sarker,³ and purified by fractionally distilling between 33.5 and 34.5°C. METHYL PROPIOLATE was prepared by a straight-forward esterification between propiolic acid and methanol. The pure ester was separated using an Aerograph Autoprop 705 gas-liquid chromatograph fitted with a 20 ft column packed with S.E. 30, at a column temperature of 60°C. METHYL CYANOFORMATE was prepared by direct exchange between potassium cyanide and methyl chloroformate according to the general method suggested by Giuud, Nussler and Keller,⁴ and the fraction distilling between 97 and 100°C was retained. Infra-red spectroscopy and gas-liquid chromatography indicated the presence of less than 1 % methyl chloroformate and the final sample was used with a small amount of methyl chloroformate as the only impurity. A sample of METHYL ACRYLATE was obtained from Koch-Lights Chemical Co. (*puriss.* grade) and its purity established by gas-liquid chromatography. The sample used was stabilized against polymerization by the presence of 0.1 % hydroquinone, and was normally stored in the dark at about -70°C . Laboratory reagent-grade METHYL ACETATE was obtained from B.D.H. Chemicals Ltd. and was purified from traces of methanol by gas-liquid chromatography. Deuterated methyl acetates, $\text{CD}_3\text{COOCD}_3$, $\text{CD}_3\text{COOCH}_3$ and $\text{CH}_3\text{COOCD}_3$ were prepared by esterification of the appropriate acid with CD_3OH , CH_3OH and CD_3OH respectively with concentrated sulphuric acid as a catalyst. In each case the distillate was purified by gas-liquid chromatography.

ANALYSIS OF SPECTRA

METHYL FLUOROFORMATE

The rotational spectrum of methyl fluoroformate consisted of strong μ_A type lines and much weaker μ_B lines. Low J R branches of the former were readily

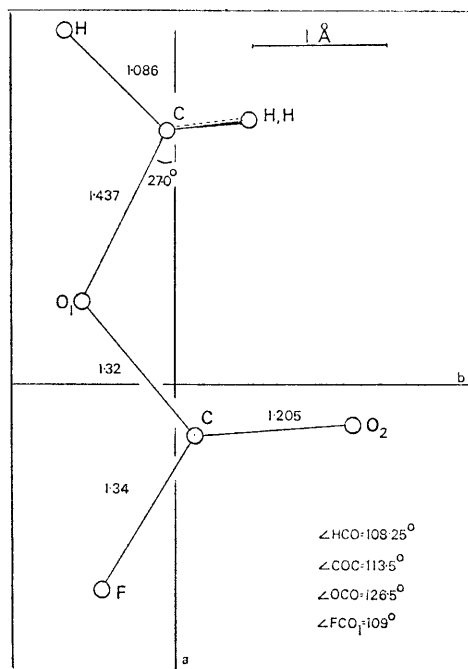


Fig. 1.—Approximate structure of methyl fluoroformate.

assigned from their Stark effects, yielding precise values for the rotational constants B and C . An accurate value of the A rotational constant was obtained only after careful searching revealed several μ_B transitions. The latter were split into doublets of about 5 MHz separation, owing to interaction of the overall rotation and the internal motion of the methyl group. Similar fine structure of 1 MHz or less was later measured on some of the μ_A lines. The observed absorption frequencies are tabulated in table 1 together with the differences between the experimental values and those calculated for a rigid rotor with rotational constants as shown in table 6. Small divergencies caused by centrifugal distortion were observed for higher J transitions.

TABLE 1.—ROTATIONAL SPECTRUM OF METHYL FLUOROFORMATE

R-BRANCH LINES

transition	symmetry species	obs. frequency (MHz) ($\nu_{\text{obs.}}$)	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$
$1_{11}-2_{12}$	A	14 022.93	0.02
	E	14 023.72	
$1_{01}-2_{02}$	A	15 066.29	−0.03
	E	15 066.03	
$1_{10}-2_{11}$	A	16 400.47	0.01
	E	16 399.11	
$2_{12}-3_{13}$	A	20 948.34	−0.12
	E		
$2_{02}-3_{03}$	A	22 249.83	−0.10
	E	22 249.27	
$2_{21}-3_{22}$	A	22 817.42	−0.10
	E		
$2_{20}-3_{21}$	A	23 384.86	−0.26
	E		
$2_{11}-3_{12}$	A	24 503.52	−0.05
	E	24 502.75	
$3_{13}-4_{14}$	A	27 785.34	−0.38
	E		
$3_{03}-4_{04}$	A	29 083.89	−0.20
	E	29 082.95	
$3_{22}-4_{23}$	A	30 309.62	−0.26
	E		
$3_{31}-4_{32}$	A	30 683.18	−0.27
	E		
$3_{30}-4_{31}$	A	30 749.43	−0.62
	E		
$3_{21}-4_{22}$	A	31 648.17	−0.27
	E		
$3_{12}-4_{13}$	A	32 474.12	−0.09
	E	32 473.12	
$4_{14}-5_{15}$	A	34 526.62	−0.50
	E	34 526.34	
$4_{04}-5_{05}$	A	35 608.94	0.27
	E	35 607.73	
$4_{23}-5_{24}$	A	37 706.98	0.41
	E	37 708.01	
$4_{32}-5_{33}$	A	38 421.65	−0.50
	E		

TABLE 1.—Continued

R-BRANCH LINES

transition	symmetry species	obs. frequency (MHz) ($\nu_{\text{obs.}}$)	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$
$4_{31}-5_{32}$	<i>A</i>	38 649.54	−0.75
	<i>E</i>	38 601.24	
$4_{22}-5_{23}$	<i>A</i>	40 120.87	−0.56
	<i>E</i>	40 119.04	
$4_{13}-5_{14}$	<i>A</i>	40 242.50	−0.30
	<i>E</i>	40 241.16	
$2_{02}-3_{13}$	<i>A</i>	26 565.32	0.01
	<i>E</i>	26 560.30	

Q-BRANCH LINES

$8_{17}-8_{26}$	<i>A</i>	24 807.66	0.18
	<i>E</i>	24 801.27	
$8_{26}-8_{35}$	<i>A</i>	27 919.27	−0.57
	<i>E</i>	27 900.43	
$9_{27}-9_{36}$	<i>A</i>	27 322.92	−0.50
	<i>E</i>	27 305.87	
$10_{28}-10_{37}$	<i>A</i>	28 025.96	−1.23
	<i>E</i>	28 012.13	
$11_{29}-11_{38}$	<i>A</i>	30 282.41	−1.68
	<i>E</i>	30 272.21	
$12_{2,10}-12_{39}$	<i>A</i>	34 210.40	−2.54
	<i>E</i>		
$11_{38}-11_{47}$	<i>A</i>	39 106.65	−2.14
	<i>E</i>	39 078.74	
$12_{39}-12_{48}$	<i>A</i>	37 028.71	−2.76
	<i>E</i>	37 001.49	
$13_{3,10}-13_{49}$	<i>A</i>	36 077.79	−3.34
	<i>E</i>	36 054.13	
$14_{3,11}-14_{4,10}$	<i>A</i>	36 661.08	−4.69
	<i>E</i>	36 643.20	

The rotational constants for the non-degenerate “*A*” torsional species components (table 6) were obtained from several low *J* transitions, the frequencies of which were all explicit functions of the three rotational constants. For calculation of the internal rotation parameters, the “structural constants” were used. These are the constants which the molecule would possess if the methyl barrier were infinitely high, and for rigid rotor spectra they are easily calculable from the differences in the observed rotational constants between the *A* and *E* torsional species.

METHYL PROPIOLATE

Substitution of the heavier acetylene group for the fluorine of methyl fluoroformate results in a considerable shift of the principal axis with respect to the molecular framework. Since the polar carbonyl bond is now orientated along the intermediate axis of inertia, the μ_B transitions were expected to be more intense than the μ_A lines.

Strong μ_B *Q*-branch lines were identified using *Q*-branch diagrams. Knowing the approximate values for the constants enabled *R*-branch lines to be predicted and observed, which in turn enabled the accurate rotational constants to be obtained

(table 6). All Q -branch lines were split by internal rotation, the separation ranging from 1 to 8 MHz (table 2). The fact that no μ_A lines were observed suggests that the molecular dipole moment is orientated predominantly along the B axis.

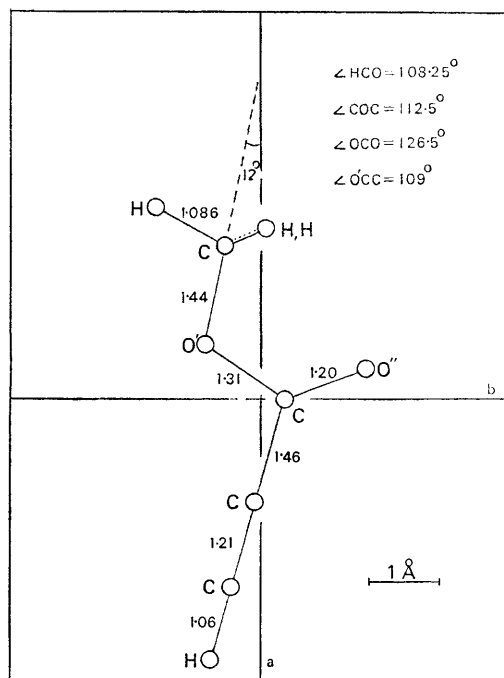


FIG. 2.—Approximate structure of methyl propiolate.

TABLE 2.—ROTATIONAL SPECTRUM OF METHYL PROPIOLATE

R-BRANCH LINES

transition	symmetry species	obs. frequency (MHz) ($\nu_{\text{obs.}}$)	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$
$1_{10}-2_{21}$	A	30 810.39	0.02
	E		
$1_{11}-2_{20}$	A	31 299.98	0.01
	E		
$1_{01}-2_{12}$	A	15 504.10	0.09
	E	$15\,502.0 \pm 0.2$	
$2_{02}-3_{13}$	A	$19\,204.0 \pm 0.5$	-0.3
	E	$19\,202.0 \pm 0.5$	
$3_{03}-4_{14}$	A	22 707.89	0.01
	E	22 705.91	
$4_{04}-5_{15}$	A	26 059.89	-0.01
	E	26 058.04	
$6_{16}-7_{07}$	A	25 962.62	-1.32
	E	25 964.02	

Table 2.—Continued

Q-BRANCH LINES

transition	symmetry species	obs. frequency (MHz) ($\nu_{\text{obs.}}$)	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$
$6_{06}-6_{15}$	<i>A</i>	13 447.21	−0.97
	<i>E</i>	13 445.67	
$7_{07}-7_{16}$	<i>A</i>	15 853.25	−1.49
	<i>E</i>	15 851.63	
$10_{0,10}-10_{19}$	<i>A</i>	25 840.75	−3.94
	<i>E</i>	25 839.17	
$11_{0,11}-11_{1,10}$	<i>A</i>	29 899.85	−4.95
	<i>E</i>	29 898.23	
$5_{15}-5_{24}$	<i>A</i>	25 843.91	−0.25
	<i>E</i>	25 836.55	
$6_{16}-6_{25}$	<i>A</i>	27 306.12	−0.57
	<i>E</i>	27 299.82	
$7_{17}-7_{26}$	<i>A</i>	29 021.99	−1.07
	<i>E</i>	29 015.95	
$8_{18}-8_{27}$	<i>A</i>	30 989.68	1.44
	<i>E</i>	30 983.84	
$6_{15}-6_{24}$	<i>A</i>	19 021.81	0.35
	<i>E</i>	19 017.39	
$7_{16}-7_{25}$	<i>A</i>	18 646.13	0.20
	<i>E</i>	18 641.58	
$8_{17}-8_{26}$	<i>A</i>	18 572.06	−1.78
	<i>E</i>	18 567.77	
$9_{18}-9_{27}$	<i>A</i>	18 884.39	−2.37
	<i>E</i>	18 880.40	
$10_{19}-10_{28}$	<i>A</i>	19 648.79	−3.05
	<i>E</i>	19 645.19	
$11_{1,10}-11_{29}$	<i>A</i>	20 921.5 ± 2	−2.0
	<i>E</i>	20 918.5 ± 2	
$14_{1,13}-14_{2,12}$	<i>A</i>	28 087.95	−6.79
	<i>E</i>	28 086.54	
$10_{28}-10_{37}$	<i>A</i>	32 103.67	0.11
	<i>E</i>	32 096.40	
$11_{29}-11_{38}$	<i>A</i>	30 868.61	0.13
	<i>E</i>	30 860.52	
$12_{2,10}-12_{3,9}$	<i>A</i>	29 742.47	0.04
	<i>E</i>	29 734.21	
$13_{2,11}-13_{3,10}$	<i>A</i>	28 849.69	−0.32
	<i>E</i>	28 841.79	
$14_{2,12}-14_{3,11}$	<i>A</i>	28 307.20	−1.07
	<i>E</i>	28 299.81	
$15_{2,13}-15_{3,12}$	<i>A</i>	28 216.03	−2.25
	<i>E</i>	28 209.52	
$16_{2,14}-16_{3,13}$	<i>A</i>	28 657.68	−3.87
	<i>E</i>	28 652.02	
$17_{2,15}-17_{3,14}$	<i>A</i>	29 693.92	−6.27
	<i>E</i>	29 689.41	
$18_{2,16}-18_{3,15}$	<i>A</i>	31 367.24	−8.97
	<i>E</i>	31 363.90	

METHYL CYANOFORMATE

Although the methyl cyanoformate molecule has similar rotational constants to those of methyl propiolate, the presence of the electronegative CN group would be expected to swing the orientation of the dipole moment towards the *A* axis as compared

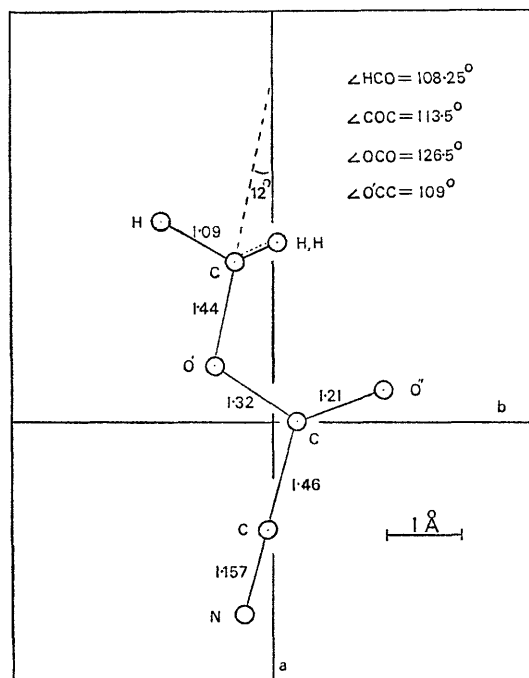


FIG. 3.—Approximate structure of methyl cyanoformate.

TABLE 3.—ROTATIONAL SPECTRUM OF METHYL CYANOFORMATE

R-BRANCH LINES

transition	symmetry species	obs. frequency (MHz) ($\nu_{\text{obs.}}$)	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$
1 ₁₁ -2 ₁₂		8 416.4 ± 1.0	0.8
1 ₀₁ -2 ₀₂		8 874.33	0.17
1 ₁₀ -2 ₁₁		9 380.0 ± 1.0	-0.3
2 ₁₂ -3 ₁₃		12 608.91	-0.02
2 ₀₂ -3 ₀₃		13 252.21	0.04
2 ₁₁ -3 ₁₂		14 055.12	-0.02
3 ₁₃ -4 ₁₄		16 785.52	-0.31
3 ₀₃ -4 ₀₄		17 561.24	-0.25
3 ₁₂ -4 ₁₃		18 710.77	0.09
4 ₁₄ -5 ₁₅		20 942.03	-0.43
4 ₀₄ -5 ₀₅		21 785.34	-0.44
4 ₁₃ -5 ₁₄		23 338.76	0.08
5 ₁₅ -6 ₁₆		25 075.62	-0.62
5 ₀₅ -6 ₀₆		25 917.89	-0.69
5 ₂₃ -6 ₂₄	<i>A</i>	27 361.64	0.07
	<i>E</i>	27 360.24	0.05
5 ₁₄ -6 ₁₅		27 929.48	0.02

TABLE 3.—Continued

Q-BRANCH LINES

transition	symmetry species	obs. frequency (MHz) ($\nu_{\text{obs.}}$)	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$
$7_{16}-7_{25}$	<i>A</i>	18 384.95	0.00
	<i>E</i>	18 379.54	
$8_{17}-8_{26}$	<i>A</i>	18 373.86	0.09
	<i>E</i>	18 368.01	
$9_{18}-9_{27}$	<i>A</i>	18 774.39	0.71
	<i>E</i>	18 768.68	
$10_{19}-10_{28}$	<i>A</i>	19 653.69	1.09
	<i>E</i>	19 648.65	
$11_{1,10}-11_{29}$	<i>A</i>	21 066.99	1.65
	<i>E</i>	21 062.58	
$12_{1,11}-12_{2,10}$	<i>A</i>	23 053.66	2.00
	<i>E</i>	23 050.03	
$13_{1,12}-13_{2,11}$	<i>A</i>	25 632.16	2.49
	<i>E</i>	25 629.44	
$11_{29}-11_{38}$	<i>A</i>	30 201.56	−2.13
	<i>E</i>	30 190.50	
$12_{2,10}-12_{39}$	<i>A</i>	29 113.58	−2.06
	<i>E</i>	29 101.99	
$13_{2,11}-13_{3,10}$	<i>A</i>	28 300.56	−1.88
	<i>E</i>	28 289.33	
$14_{2,12}-14_{3,11}$	<i>A</i>	27 881.73	−1.69
	<i>E</i>	27 871.45	
$15_{2,13}-15_{3,12}$	<i>A</i>	27 957.53	−1.45
	<i>E</i>	27 948.64	
$16_{2,14}-16_{3,13}$	<i>A</i>	28 607.12	−1.11
	<i>E</i>	28 599.49	
$17_{2,15}-17_{3,14}$	<i>A</i>	29 888.42	−1.27
	<i>E</i>	29 882.53	

with that found in methyl propiolate. This would result in the presence of strong μ_A lines.

Several strong low $J \mu_A$ transitions were assigned without difficulty from their Stark effects, although only one of the $\mu_A J(1 \rightarrow 2)$ lines was strong enough to be measured. Values for the rotational constants *B* and *C* were obtained from the three transitions, $1_{01} \rightarrow 2_{02}$, $2_{11} \rightarrow 3_{12}$ and $2_{12} \rightarrow 3_{13}$ (each of which is an explicit function of the three rotational constants) while the value of *A* was arbitrarily fixed at 9570 MHz.

A fairly accurate value for *A* was eventually obtained when the $9_{18} \rightarrow 9_{27}$, $10_{19} \rightarrow 10_{28}$ and $11_{10} \rightarrow 11_{29} \mu_B$ lines were measured and assigned. The measured transitions and the rotational constants are listed in table 3 and 6 respectively. The relative weakness of μ_B lines suggested that μ_B was much smaller than μ_A . All observed μ_B lines were split into doublets by internal rotation. No nitrogen quadrupole coupling effects were seen on any spectral lines.

METHYL ACRYLATE

Methyl acrylate differs from the other compounds studied because it has an additional internal axis of rotation which could give rise to separate rotational isomers (fig. 4). The most likely isomers, planar *cis* and *trans*, would be expected to have different rotational spectra since the *cis* structure is close to being a prolate

Assignment of most of the strong absorptions was by Q -branch diagrams and subsequently looking for R -branch lines. Accurate values of the rotational constants

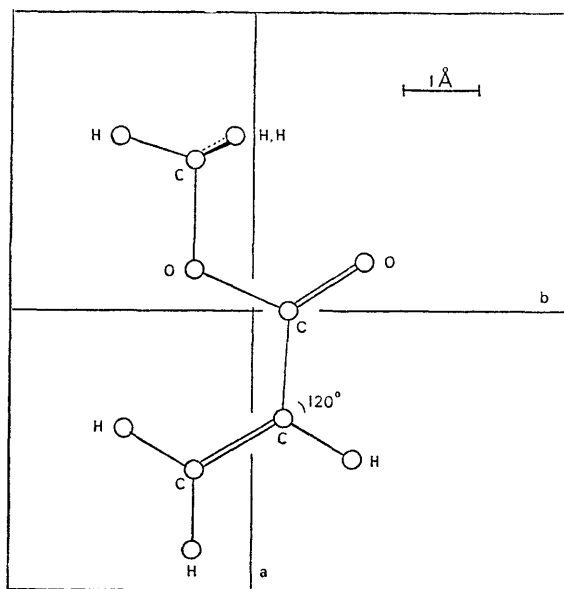


FIG. 4.—Approximate structures of (a) *cis* and (b) *trans* methyl acrylate. The bond lengths, and all unspecified angles, are identical to those used for the model of the *cis* rotamer (fig. 4a).

were obtained using a least squares fit of low J transitions. The assigned lines were all of μ_B type (table 4) and the rotational constants correspond closely to those predicted for the cis conformation (table 6).

A series of prominent satellite lines were identified and several transitions were assigned to the $V = 1$ and $V = 2$ excited vibrational states of the C—C torsional mode of the cis molecular conformer (table 4). Although a number of non-cis weak lines (many doublets) were observed, it was not possible to fit these into any predictable pattern corresponding to the trans rotamer.

TABLE 4.—ROTATIONAL SPECTRUM OF METHYL ACRYLATE (cis)
GROUND STATE ($V = 0$)

R-BRANCH LINES

transition	symmetry species	obs. frequency (MHz) ($\nu_{\text{obs.}}$)	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$
1 ₁₁ -2 ₂₀	<i>A</i>	33 248.07	0.07
	<i>E</i>		
1 ₁₀ -2 ₂₁	<i>A</i>	32 827.89	-0.30
	<i>E</i>		
1 ₀₁ -2 ₁₂	<i>A</i>	16 068.81	-0.03
	<i>E</i>	16 066.19	
2 ₀₂ -3 ₁₃	<i>A</i>	19 716.85	0.03
	<i>E</i>	19 714.45	
3 ₀₃ -4 ₁₄	<i>A</i>	23 187.55	0.03
	<i>E</i>	23 185.25	
4 ₀₄ -5 ₁₅	<i>A</i>	26 511.72	-0.02
	<i>E</i>	26 509.54	
6 ₀₆ -7 ₁₇	<i>A</i>	32 891.06	-0.05
	<i>E</i>	32 889.11	
4 ₁₄ -5 ₀₅	<i>A</i>	14 613.42	0.00
	<i>E</i>	14 615.58	
5 ₁₅ -6 ₀₆	<i>A</i>	19 432.62	0.03
	<i>E</i>	19 434.51	
6 ₁₆ -7 ₁₇	<i>A</i>	24 226.17	-0.03
	<i>E</i>	24 227.87	

Q-BRANCH LINES

$J_{1(J-1)}-J_{2(J-2)}$

5	<i>A</i>	22 079.04	-0.21
	<i>E</i>	22 075.71	
6	<i>A</i>	21 431.31	-0.26
	<i>E</i>	21 426.56	
7	<i>A</i>	20 897.61	-0.29
	<i>E</i>	20 892.40	
8	<i>A</i>	20 557.11	-0.39
	<i>E</i>	20 551.73	
9	<i>A</i>	20 482.47	-0.48
	<i>E</i>	20 477.30	
10	<i>A</i>	20 736.45	-0.60
	<i>E</i>	20 731.52	
11	<i>A</i>	21 371.87	-0.77
	<i>E</i>	21 367.26	
12	<i>A</i>	22 432.87	-0.98
	<i>E</i>	22 428.64	

TABLE 4.—Continued

transition	symmetry species	obs. frequency (MHz) ($\nu_{\text{obs.}}$)	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$
13	<i>A</i>	23 954.96	−1.35
	<i>E</i>	23 951.15	
14	<i>A</i>	25 963.34	−1.75
	<i>E</i>	25 959.91	
15	<i>A</i>	28 468.14	−2.25
	<i>E</i>	28 465.13	
16	<i>A</i>	31 459.93	−2.79
	<i>E</i>	31 457.20	
<i>J</i> _{0<i>J</i>} - <i>J</i> _{1(<i>J</i>-1)}			
7	<i>A</i>	15 187.77	−0.23
	<i>E</i>	15 185.48	
8	<i>A</i>	17 580.12	−0.37
	<i>E</i>	17 577.83	
9	<i>A</i>	20 391.57	−0.50
	<i>E</i>	20 389.15	
10	<i>A</i>	23 602.30	−0.78
	<i>E</i>	23 599.81	
<i>J</i> _{2(<i>J</i>-2)} - <i>J</i> _{3(<i>J</i>-3)}			
13	<i>A</i>	33 423.81	−1.37
	<i>E</i>	33 414.41	
14	<i>A</i>	32 407.23	−1.58
	<i>E</i>	32 397.87	
15	<i>A</i>	31 631.31	−1.72
	<i>E</i>	31 622.17	
16	<i>A</i>	31 182.50	−2.01
	<i>E</i>	31 174.00	
17	<i>A</i>	31 135.65	−2.42
	<i>E</i>	31 127.86	
EXCITED VIBRATIONAL STATE (<i>V</i> = 1)			
<i>R</i> -BRANCH LINES			
2 ₀₂ -3 ₁₃	<i>A</i>	19 631.54	−0.01
	<i>E</i>		
3 ₀₃ -4 ₁₄	<i>A</i>	23 114.05	0.03
	<i>E</i>	23 111.78 ± 2	
4 ₀₄ -5 ₁₅	<i>A</i>	26 451.36	−0.02
	<i>E</i>	26 449.23	
5 ₁₅ -6 ₀₆	<i>A</i>	19 561.58	0.03
	<i>E</i>	19 563.39	
6 ₁₆ -7 ₀₇	<i>A</i>	24 353.66	0.03
	<i>E</i>	24 355.36	
<i>Q</i> -BRANCH LINES			
7 ₀₇ -7 ₁₆	<i>A</i>	15 036.65	0.90
	<i>E</i>	15 034.43	
8 ₀₈ -8 ₁₇	<i>A</i>	17 416.20	0.95
	<i>E</i>	17 414.06	
7 ₁₆ -7 ₂₅	<i>A</i>	20 599.47	0.08
	<i>E</i>	20 594.39	

TABLE 4.—Continued

transition	symmetry species	obs. frequency (MHz) ($\nu_{\text{obs.}}$)	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$
$8_{17}-8_{26}$	<i>A</i>	20 268.87	0.06
	<i>E</i>	20 263.71	
$10_{19}-10_{28}$	<i>A</i>	20 468.19	0.25
	<i>E</i>	20 463.30	
$11_{1,10}-11_{2,9}$	<i>A</i>	21 112.48	0.21
	<i>E</i>	21 108.05	
$12_{1,11}-12_{2,10}$	<i>A</i>	22 181.17	0.30
	<i>E</i>	22 177.13	
$13_{1,12}-13_{2,11}$	<i>A</i>	$23\ 709.36 \pm 0.2$	0.46
	<i>E</i>	23 705.60	
$14_{1,13}-14_{2,12}$	<i>A</i>	$25\ 721.04 \pm 0.2$	0.28
	<i>E</i>	25 717.92	
$15_{1,14}-15_{2,13}$	<i>A</i>	28 226.19	0.40
	<i>E</i>	28 223.40	

EXCITED VIBRATIONAL STATE ($V = 2$)

$5_{15}-6_{06}$	<i>A</i>	19 686.41	0.0
	<i>E</i>	19 688.22	
$9_{18}-9_{27}$	<i>A</i>	19 936.48	-0.03
	<i>E</i>	19 931.55	
$11_{1,10}-11_{2,9}$	<i>A</i>	20 862.58	0.01
	<i>E</i>	20 858.06	
$12_{1,11}-12_{2,10}$	<i>A</i>	21 938.55	0.02
	<i>E</i>	21 934.41	
$13_{1,12}-13_{2,11}$	<i>A</i>	23 472.17	0.0
	<i>E</i>	23 468.64	
$14_{1,13}-14_{2,12}$	<i>A</i>	25 487.32	0.05
	<i>E</i>	25 484.12	
$15_{1,14}-15_{2,13}$	<i>A</i>	27 992.23	-0.05
	<i>E</i>	27 989.40	

METHYL ACETATE

The presence of two non-equivalent methyl groups in methyl acetate results in the analysis of its microwave spectrum being a more difficult problem. The methoxy CH_3 barrier, by analogy with the other esters, was expected to cause most absorption lines to appear as doublets split by a few MHz. On the other hand, the acetyl CH_3 group would be likely to have a considerably lower barrier to internal rotation, possibly close to the value found for acetic acid [483 cal/mol⁴]. Such a value would give rise to large splittings of the *A* and *E* components of each absorption line, thus making ready identification of each component more difficult. When CH_3 groups are replaced by CD_3 the greater inertia of the latter generally results in a large reduction in the internal rotation splitting. For methyl acetate this effect would remove entirely the splitting due to the methoxy CH_3 group and greatly reduce the acetyl CH_3 splitting. Consequently, a study of the microwave spectra of the species $\text{CD}_3\text{COOCH}_3$, $\text{CH}_3\text{COOCD}_3$ and $\text{CD}_3\text{COOCD}_3$ was carried out; later, confirmation of the assignment of the more prominent features in the spectrum of $\text{CH}_3\text{COOCH}_3$ was possible only after consideration of the spectra of all three isotopically substituted derivatives. In this attempt to interpret the spectrum of methyl acetate no account has been taken of the possible coupling between the two

methyl groups and the results should be treated with the caution normally extended to "first-order" treatments.

$\text{CH}_3\text{COOCH}_3$.—A series of symmetrical doublets was readily identified as belonging to the μ_B Q -branch series $J_{1,J-1} \rightarrow J_{2,J-2}$, and this enabled other lines to be predicted and measured. Assignment of R -branch lines was not easy, but eventually the three $J(1 \rightarrow 2)$ μ_B transitions were found as weak absorptions. Measurements of other lines confirming the assignment was carried out in due course (table 5).

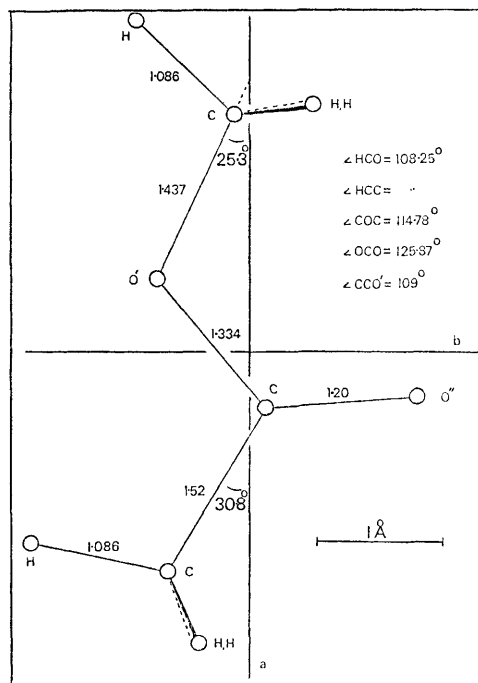


FIG. 5.—Approximate structure of methyl acetate.

These assigned lines (most of which were doublets) were attributed to the A torsional species of the acetyl CH_3 group, the observed constants for which (table 6) predict a spectrum close to that of a rigid rotor. The differences between observed and calculated frequencies show an unusually large deviation for medium and high J lines (table 5) which is indicative of large centrifugal forces. No corresponding sets of lines assignable to the E species were observed.

TABLE 5.—ROTATIONAL SPECTRUM OF METHYL ACETATE

(a) $\text{CH}_3\text{COOCH}_3$

R -BRANCH LINES

transition	symmetry species	obs. frequency (MHz) ($\nu_{\text{obs.}}$)	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$
$1_{11}-2_{20}$	A	35 530.50	0.02
	E		
$1_{10}-2_{21}$	A	34 297.61	0.01
	E		
$1_{01}-2_{12}$	A	19 638.35	0.0
	E		

TABLE 5.—Continued

transition	symmetry species	obs. frequency (MHz) ($\nu_{\text{obs.}}$)	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$
$2_{02}-3_{13}$	<i>A</i>	25 296.4 \pm 0.5	−0.9
	<i>E</i>	25 293.9 \pm 0.5	
$3_{03}-4_{14}$	<i>A</i>	30 632.00	−1.49
	<i>E</i>	30 629.75	
$4_{04}-5_{15}$	<i>A</i>	35 877.74	−2.49
	<i>E</i>	35 876.00	
$3_{13}-4_{04}$	<i>A</i>	23 729.83	−3.15
	<i>E</i>	23 731.59	
$4_{14}-5_{05}$	<i>A</i>	31 197.45 \pm 1	−4.0
	<i>E</i>	31 198.95 \pm 1	
$5_{15}-6_{06}$	<i>A</i>	38 302.3 \pm 1	−3.4
	<i>E</i>		

Q-BRANCH LINES

$5_{05}-5_{14}$	<i>A</i>	18 051.54	−0.40
	<i>E</i>	18 049.14	
$6_{06}-6_{15}$	<i>A</i>	23 387.00	−1.13
	<i>E</i>	23 384.32	
$7_{07}-7_{16}$	<i>A</i>	29 494.78	−2.10
	<i>E</i>	29 491.61	
$8_{08}-8_{17}$	<i>A</i>	36 001.35	−3.31
	<i>E</i>	35 997.03	
$9_{27}-9_{36}$	<i>A</i>	25 529.40	−11.07
	<i>E</i>	25 520.64	
$10_{28}-10_{37}$	<i>A</i>	26 116.50	−12.12
	<i>E</i>	26 109.37	
$11_{29}-11_{38}$	<i>A</i>	28 131.46	−12.85
	<i>E</i>	28 126.34	
$12_{39}-12_{48}$	<i>A</i>	34 671.33	−35.84
	<i>E</i>	34 657.25	
$13_{3,10}-13_{49}$	<i>A</i>	33 707.84	−35.68
	<i>E</i>	33 695.95	
$3_{12}-3_{21}$	<i>A</i>	17 782.7 \pm 0.3	0.6
	<i>E</i>	17 778.81	
$4_{13}-4_{22}$	<i>A</i>	17 005.60	0.26
	<i>E</i>	17 000.10	
$5_{14}-5_{23}$	<i>A</i>	16 871.62	−0.73
	<i>E</i>	16 866.13	
$6_{15}-6_{24}$	<i>A</i>	17 690.00	−1.79
	<i>E</i>	17 685.21	
$7_{16}-7_{25}$	<i>A</i>	19 687.02	−3.45
	<i>E</i>	19 682.94	
$8_{17}-8_{26}$	<i>A</i>	23 010.26	−4.13
	<i>E</i>	23 007.08	
$9_{18}-9_{27}$	<i>A</i>	27 673.14	−5.68
	<i>E</i>	27 670.69	

TABLE 5.—Continued

(b) $\text{CD}_3\text{COOCH}_3$			
<i>R</i> -BRANCH LINES			
transition	symmetry species	obs. frequency (MHz) ($\nu_{\text{obs.}}$)	$\nu_{\text{obs}} - \nu_{\text{calc.}}$
$1_{11}-2_{20}$	<i>A</i>	32 226.45	0.20
$1_{01}-2_{12}$	<i>A</i>	17 879.54	−0.20
$3_{03}-4_{14}$	<i>A</i>	27 971.87	−3.00
	<i>E</i>	27 969.82	
$3_{13}-4_{04}$	<i>A</i>	21 254.52	−5.91
	<i>E</i>	21 255.64	
$4_{14}-5_{05}$	<i>A</i>	28 060.88	−6.81
	<i>E</i>	28 062.13	
<i>Q</i> -BRANCH LINES			
$4_{13}-4_{22}$	<i>A</i>	15 689.54	0.82
	<i>E</i>	15 684.99	
$5_{14}-5_{23}$	<i>A</i>	15 422.13	−0.24
	<i>E</i>	15 417.32	
$6_{15}-6_{24}$	<i>A</i>	15 892.09	−1.38
	<i>E</i>	15 887.85	
$7_{16}-7_{25}$	<i>A</i>	$17\,296.20 \pm 0.5$	−2.60
	<i>E</i>	$17\,292.78 \pm 0.5$	
$8_{17}-8_{26}$	<i>A</i>	19 773.38	−3.55
	<i>E</i>	19 770.48	
$6_{06}-6_{15}$	<i>A</i>	19 872.39	0.24
	<i>E</i>	19 870.35	
(c) $\text{CD}_3\text{COOCD}_3$			
<i>R</i> -BRANCH LINES			
$1_{11}-2_{20}$		30 266.58	0.0
$1_{10}-2_{21}$		29 453.37	0.0
$1_{01}-2_{12}$		16 665.06	0.0
$2_{02}-3_{13}$		21 454.94	−1.00
$3_{03}-4_{14}$		25 990.05	−1.95
$4_{04}-5_{15}$		30 401.04	−3.06
$5_{05}-6_{16}$		34 825.52	−4.26
$4_{14}-5_{05}$		25 036.97	−5.80
$6_{16}-7_{07}$	<i>A</i>	36 905.41	−7.00
	<i>E</i>	36 937.20	
<i>Q</i> -BRANCH LINES			
$6_{06}-6_{15}$	<i>A</i>	16 804.07	−1.95
	<i>E</i>	16 711.83	
$7_{07}-7_{16}$	<i>A</i>	21 005.10	−3.33
	<i>E</i>	20 889.21	
$8_{08}-8_{17}$	<i>A</i>	25 711.54	−4.90
	<i>E</i>	25 589.54	
$9_{09}-9_{18}$	<i>A</i>	30 701.32	−6.67
	<i>E</i>	30 554.04	
$10_{10}-10_{19}$	<i>A</i>	35 769.63	−9.40
	<i>E</i>	35 574.33	
$4_{11}-4_{23}$	<i>A</i>	21 902.25	0.42
$5_{15}-5_{24}$	<i>A</i>	23 871.28	−0.91
$8_{18}-8_{27}$	<i>A</i>	32 122.03	−5.72

TABLE 5.—Continued

$J_1(J-1)-J_2(J-2)$	transition	symmetry species	obs. frequency (MHz) ($\nu_{\text{obs.}}$)	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$
4		<i>A</i>	15 482.33	1.11
5		<i>A</i>	15 039.18	0.20
6		<i>A</i>	15 103.05	-1.07
7		<i>A</i>	15 843.87	-2.41
		<i>E</i>	15 770.53	
8		<i>A</i>	17 389.69	-4.05
		<i>E</i>	17 300.50	
9		<i>A</i>	19 827.08	-5.91
		<i>E</i>	19 737.28	
10		<i>A</i>	23 177.37	-7.88
		<i>E</i>	23 088.82	
11		<i>A</i>	27 366.01	-10.33
		<i>E</i>	27 272.06	
12		<i>A</i>	32 218.79	-13.32
		<i>E</i>	32 106.99	
13		<i>A</i>	37 494.53	-17.52
		<i>E</i>	37 349.70	

(d) $\text{CH}_3\text{COOCD}_3$

$1_{01}-2_{12}$	18 244.52	-0.19
$2_{02}-3_{13}$	23 462.09	-0.74
$3_{03}-4_{14}$	28 389.83	-1.17
$3_{13}-4_{04}$	20 903.40	-3.22
$4_{14}-5_{05}$	27 780.39	-3.67
$4_{13}-4_{22}$	16 706.25	0.10
$5_{14}-5_{23}$	16 309.34	-0.62
$6_{15}-6_{24}$	16 569.04	-1.78
$7_{16}-7_{25}$	17 681.47	-3.44
$8_{17}-8_{26}$	19 791.34	-5.44
$6_{06}-6_{15}$	19 551.46	-4.28

$\text{CD}_3\text{COOCH}_3$.—The assignment of the rotational spectrum of $\text{CD}_3\text{COOCH}_3$ followed a similar pattern to that of $\text{CH}_3\text{COOCH}_3$. Most absorption lines retained the doublet feature which can be attributed to the presence of the methoxy CH_3 group. Although deuterating the acetyl CH_3 top should have the effect of reducing the internal rotation splitting due to this group only one set of doublets was observed in the spectrum (table 5) and this was assigned to the acetyl *A* torsional species (table 6).

$\text{CH}_3\text{COOCD}_3$.—The spectral assignment of the *A* acetyl CH_3 torsional species of this molecular species was straight-forward, since the deuterio methoxy group produced no splitting of the rotational lines. The absorption lines are tabulated in table 5. The lines due to the *E* torsional species of the acetyl group were too far removed from a predicted rigid rotor spectrum for any transitions to be identified.

$\text{CD}_3\text{COOCD}_3$.—The rotational spectrum of this species was assigned following the same procedure as with the previous molecules. All the observed lines were singlets. A search was carried out for additional lines due to the presence of the acetyl CD_3 group since $\text{CD}_3\text{COOCD}_3$ represented the most favourable species for observing such lines. With a predicted barrier height similar to the value in acetic

TABLE 6.—ROTATIONAL CONSTANTS OF METHYL FLUOROFORMATE, PROPIOLATE, CYANOFORMATE, ACETATE AND ACRYLATE

	<i>A</i> (MHz)	<i>B</i> (MHz)	<i>C</i> (MHz)	κ	$\frac{\text{inertial}^a \text{ defect,}}{4mc^2 - (I_A + I_B - I_C)}$ a.m.u. Å ²
METHYL FLUOROFORMATE					
methoxy CH ₃ <i>A</i> -torsional species	11 057.56 ± 0.1	4397.31 ± 0.05	3208.54 ± 0.05	−0.6971	
observed “ structural ”	11 054.19 ± 0.1	4397.22 ± 0.05	3208.54 ± 0.05	−0.6970	+ 0.06
METHYL PROPIOLATE					
methoxy CH ₃ <i>A</i> -torsional species	9 615.89 ± 0.1	2430.23 ± 0.1	1962.71 ± 0.1	−0.8778	
observed “ structural ”	9 614.64 ± 0.1	2430.23 ± 0.1	1962.71 ± 0.1	−0.8778	+ 0.17
METHYL CYANOFORMATE					
methoxy CH ₃ <i>A</i> -torsional species	9 555.02 ± 0.5	2465.64 ± 0.2	1983.33 ± 0.2	−0.8726	
observed “ structural ”	9 553.18 ± 0.5	2465.64 ± 0.2	1983.33 ± 0.2	−0.8726	+ 0.14
METHYL ACETATE					
CH ₃ COOCH ₃					
<i>A</i> -species of both acetyl and methoxy CH ₃	10 406.81	4176.93	3077.18	−0.6999	
<i>A</i> -species of acetyl CH ₃ , structural					
methoxy CH ₃	10 405.16	4176.89	3077.18	−0.6999	+ 1.07
CH ₃ COOCD ₃					
<i>A</i> -species of acetyl CH ₃	8 961.88	3312.12	2657.73	−0.7672	+ 0.64
observed “ structural ” constants					
(approximate)	8 923.2	3310.0	2567.7	−0.7664	

TABLE 6.—Continued

	<i>A</i> (MHz)	<i>B</i> (MHz)	<i>C</i> (MHz)	kappa	inertial* defect, $4mc^2 - (I_A + I_B - I_C)$ a.m.u. Å ²
CD ₃ COOCH ₃					
<i>A</i> -species of both acetyl and methoxy CH ₃	9 468.07	3720.83	2803.89	-0.7248	
<i>A</i> -species of acetyl CH ₃ , structural methoxy CH ₃	9 466.68	3720.81	2803.89	-0.7248	+0.63
CD ₃ COOCD ₃					
<i>A</i> -species of acetyl CH ₃	9 808.09	3696.84	2812.21	-0.7471	+1.07
METHYL ACRYLATE					
<i>V</i> = 0					
methoxy CH ₃ <i>A</i> -torsional species observed "structural "	10 301.98 10 300.49	2327.08 2327.06	1922.29 1922.29	-0.9034 -0.9034	-0.16
<i>V</i> = 1					
methoxy CH ₃ <i>A</i> -torsional species observed "structural "	10 192.88 10 191.42	2328.80 2328.78	1926.78 1926.78	-0.9027 -0.9027	-1.11
<i>V</i> = 2					
methoxy CH ₃ <i>A</i> -torsional species observed "structural "	10 088.05 10 086.60	2330.53 2330.51	1931.16 1931.16	-0.9021 -0.9021	-2.06

Rotational constants are believed accurate to ± 0.05 MHz, except where otherwise indicated.
 * for methyl acetate the expression used was $8 mc^2 - (I_A + I_B - I_C)$.

acid (483 cal/mol)⁵ the search was unsuccessful. Eventually, however, a series of lines separated from the main absorptions by between 70 and 200 MHz was found. Twelve lines, ranging from $J = 6$ to $J = 13$ were assigned to acetyl E species transitions (table 5). These were approximately a factor of two more intense than the A torsional species transitions and they possessed faster Stark effects. An intensity ratio of 9:16 is expected for the A and E torsional species respectively for a CD_3 group as a result of the relative nuclear spin statistical weights.⁶

DIPOLE MOMENTS

The dipole moments of methyl fluoroformate and methyl cyanoformate were measured using a d.c. voltage generator (accurate to 1 part in 1000) with a small 100 kHz square wave modulation superimposed on the d.c. voltage. This has the effect of splitting each Stark lobe into two components. The amplitude of the square wave modulation was kept less than $\frac{1}{3}$ of the d.c. voltage, and the average displacement of two components of each lobe was measured for every value of the applied electric field.

TABLE 7.—STARK EFFECTS AND DIPOLE MOMENTS OF METHYL FLUOROFORMATE AND METHYL CYANOFORMATE

(a) METHYL FLUOROFORMATE			
transition	M state	$\Delta\nu/E^2$ obs. (MHz V ⁻¹ cm ⁻²) $\times 10^6$	$\Delta\nu/E^2$ calc.
$1_{01}-2_{02}$	0	35.918	36.001
$1_{01}-2_{02}$	1	35.403	35.304
$2_{02}-3_{03}$	2	153.65	154.11
$\mu_a = 2.73, \quad \mu_c = 0$ (assumed), $\mu_b = 0.75, \quad \mu_t = 2.83 \pm 0.03D$.			
(b) METHYL CYANOFORMATE			
transition	M state	$\Delta\nu/E^2$ obs.	$\Delta\nu/E^2$ calc.
$5_{05}-6_{06}$	0	25.592	25.539
$5_{05}-6_{06}$	3	19.003	19.139
$5_{05}-6_{06}$	4	53.415	53.888
$\mu_a = 4.17, \quad \mu_c = 0$ (assumed), $\mu_b = 0.71, \quad \mu_t = 4.23 \pm 0.04D$.			

The cell was calibrated with OCS using a value of 0.7152 D as the dipole moment.⁷ For both esters, the transitions chosen for study exhibited little or no fine structure. For methyl fluoroformate the displacements of the $M = 0$ and $M = 1$ lobes of the $1_{01} \rightarrow 2_{02}$, and the $M = 2$ lobe of the $2_{02} \rightarrow 3_{03}$ were studied as a function of applied voltage. The data were averaged using a least-squares procedure and the total dipole moment was 2.83 ± 0.03 D (table 7). Although it was difficult to find many suitable spectral transitions for methyl cyanoformate, measurements were finally carried out on the $M = 0$, $M = 3$ and $M = 4$ lobes of the transition $5_{05} \rightarrow 6_{06}$, giving a value for the resultant dipole of 4.23 ± 0.04 D (table 7). For both methyl fluoroformate and methyl cyanoformate the observed dipole moments were significantly larger than the values predicted using tabulated bond moments.⁸

STRUCTURAL CONCLUSIONS

A study of the rotational constants and inertial defects (table 6) shows that each of the five compounds studied has a planar framework of heavy atoms. For methyl

propiolate, methyl cyanoformate and methyl acrylate the rotational constants are consistent only with the planar *cis* molecular conformation of the ester $\text{O}=\text{C}-\text{O}-\text{C}$ group. This same conclusion can be drawn for methyl acetate from a comparison of the spectra of the three deuterated compounds with that of the parent species. In the absence of any isotopic data on methyl fluoroformate, the similarity of the masses of fluorine and oxygen does not permit an unambiguous assignment of the molecular conformation, but in view of the results obtained for the other esters it would appear logical for the molecule to have the planar *cis* structure.

Molecular models for each compound (fig. 1-5) were constructed from spectroscopic and diffraction data for related molecules, with some parameters modified slightly so as to make each predicted rotational spectrum correspond more closely to the observed absorptions and internal rotation splitting patterns. These conclusions regarding the stable molecular conformations of the esters are in accordance with the findings of Curl on methyl formate.¹ The complete absence of any strong non-*cis* absorption lines places a lower limit on the energy difference between the *cis* and *trans* conformations of about 2 kcal/mol.

TABLE 8.—INTERNAL ROTATION PARAMETERS

	I_a (a.m.u. Å ²)	θ (deg.)	F (MHz)	S
methyl fluoroformate	3.20	22.0	168 790	29.74
methyl propiolate	3.20	10.5	167 901	35.15
methyl cyanoformate	3.20	5.5	168 070	32.51
methyl acetate				
$\text{CH}_3\text{COOCH}_3$	3.20	21.5	168 160	33.68
$\text{CD}_3\text{COOCH}_3$	3.20	18.3	167 405	33.66
$\text{CD}_3\text{COOCD}_3$	6.40	32.0	87 086	16.45
methyl acrylate				
$V = 0$	3.20	24.0	167 510	33.96
$V = 1$	3.20	24.0	167 400	34.02

I_a is the assumed moment of inertia of the methyl group; θ is the angle which the methyl group subtends on to the A principal axis, (the values have been modified slightly from those given in the approximate structures shown in fig 1-5 in order to improve the fit between observed and predicted spectra.); F is given by the expression $F = h^2/8\pi^2 r I_a$, where $r = 1 - \sum_i \lambda_i \rho_i$, and where λ_i is the directional cosine corresponding to θ along the three principal axes, and $\rho_i = \lambda_i I_a$.

S is a dimensionless parameter known as the reduced barrier $V_3 = (9/4)FS$.

A second conformational problem occurs with methyl acrylate. Internal rotation about the $\text{C}-\text{C}$ bond can give rise to two isomers, planar *cis* and *trans*. (The conformation of the ester group $\text{O}=\text{C}-\text{O}-\text{C}$ is considered to be firmly established in the planar *cis* position). There can be little preference *a priori* for either of these rotamers, and for acrylic acid, Bolton and co-workers have clearly demonstrated the coexistence of planar *cis* and planar *trans* rotamers.⁹ The *cis* isomer was found to be the more stable form by about 360 ± 100 cal/mol.¹⁰ Infra-red studies on methyl acrylate by Fearheller and Katon¹¹ indicate the presence of two rotamers, one of which is probably in low concentration. We have identified only the *cis* isomer in the microwave spectrum of methyl acrylate. Since the energy difference between these two forms is not likely to be large (i.e., < 1 kcal/mol) the absence of prominent lines belonging to the *trans* isomer is surprising. A probable factor contributing to the apparent lack of intensity of the *trans* species absorptions is the orientation of the

dipole moment. In *cis* methyl acrylate the orientation of the carbonyl bond lies almost exactly in the direction of the intermediate (*B*) principal axis of inertia, and it is this bond which makes the major contribution towards the overall dipole moment. The orientation of the carbonyl group for the *trans* rotamer lies at an angle of approximately 33° to the *B*-axis which would considerably reduce the intensity of the μ_B transitions.

BARRIERS TO INTERNAL ROTATION

METHOXY CH₃ BARRIERS

The presence of a methyl group in each one of the five molecules studied was shown by the fact that many absorption lines appeared as symmetrical doublets (table 9). In each case these internal rotation splittings were analyzed, and a three-fold potential barrier was determined by means of an "internal-axis" method developed by Woods.¹² In some instances, independent calculations were carried out using the "principal-axis" approach of Herschbach and co-workers.¹³ The two methods yielded essentially the same results, which are summarized in table 10. The quoted errors, which are well in excess of the experimental fit of about ± 5 cal/mol, allow for an uncertainty of $\pm 5^\circ$ in the angle θ between the methyl top and the *A* principal axis, and also for an uncertainty of ± 0.05 a.m.u. Å² in the value of I_α , the moment of inertia of the CH₃ group. The methoxy CH₃ barriers for both the deuterated and the parent species of methyl acetate (CD₃COOCH₃ and CH₃COOCH₃) were calculated from splittings observed in the spectral lines of the *A* torsional state of the acetyl CH₃ group.

TABLE 9.—OBSERVED INTERNAL ROTATION SPLITTINGS

(a) METHYL FLUOROFORMATE

transition	obs. splittings (<i>A-E</i>) (MHz)	<u>predicted splittings</u> obs. splittings
1 ₁₁ -2 ₁₂	-0.79	1.139
1 ₀₁ -2 ₀₂	0.26	1.269
1 ₁₀ -2 ₁₁	1.36	1.044
2 ₀₂ -3 ₀₃	0.56	1.143
2 ₁₁ -3 ₁₂	0.77	1.156
3 ₀₃ -4 ₀₄	0.94	1.096
3 ₁₂ -4 ₁₃	1.00	1.050
4 ₁₄ -5 ₁₅	0.28	1.643
4 ₀₄ -5 ₀₅	1.22	1.107
4 ₂₃ -5 ₂₄	-1.03	1.058
4 ₃₁ -5 ₃₂	48.30	1.000
4 ₂₂ -5 ₂₃	1.83	1.071
4 ₁₃ -5 ₁₄	1.34	1.075
2 ₀₂ -3 ₁₃	5.02	1.040
8 ₁₇ -8 ₂₆	6.39	0.986
8 ₂₆ -8 ₃₅	18.84	0.996
9 ₂₇ -9 ₃₆	17.05	1.004
10 ₂₈ -10 ₃₇	13.83	1.012
11 ₂₉ -11 ₃₈	10.20	0.999
11 ₃₈ -11 ₄₉	27.91	1.007
12 ₃₉ -12 _{4,10}	27.22	0.996
13 _{3,10} -13 _{4,11}	23.66	0.980
14 _{3,11} -14 _{4,12}	17.88	0.985

TABLE 9.—Continued

(b) METHYL PROPIOLATE

transition	obs. splittings (<i>A-E</i>) (MHz)	<u>predicted splittings</u> obs. splittings
1 ₀₁ -2 ₁₂	2.1	0.990
2 ₀₂ -3 ₁₃	2.0	0.994
3 ₀₃ -4 ₁₄	1.98	0.974
4 ₀₄ -5 ₁₅	1.85	1.011
6 ₁₆ -7 ₀₇	-1.40	0.986
6 ₀₆ -6 ₁₅	1.54	1.077
7 ₀₇ -7 ₁₆	1.62	0.963
10 _{0,10} -10 _{1,9}	1.58	0.937
11 _{0,11} -11 _{1,10}	1.62	1.018
5 ₁₅ -5 ₂₄	7.36	0.966
6 ₁₆ -6 ₂₅	6.30	1.008
7 ₁₇ -7 ₂₆	6.04	1.002
8 ₁₈ -8 ₂₇	5.84	1.004
6 ₁₅ -6 ₂₄	4.42	1.006
7 ₁₆ -7 ₂₅	4.55	0.993
8 ₁₇ -8 ₂₆	4.29	1.011
9 ₁₈ -9 ₂₇	3.99	1.004
10 ₁₉ -10 ₂₈	3.60	0.997
11 _{1,10} -11 _{2,9}	3.0	1.023
14 _{1,13} -14 _{2,12}	1.41	0.978
10 ₂₈ -10 ₃₇	7.27	1.013
11 ₂₉ -11 ₃₈	8.08	1.003
12 _{2,10} -12 _{3,9}	8.26	0.994
13 _{2,11} -13 _{3,10}	7.90	1.003
14 _{2,12} -14 _{3,11}	7.39	0.994
15 _{2,13} -15 _{3,12}	6.51	1.006
16 _{2,14} -16 _{3,13}	5.66	0.986
17 _{2,15} -17 _{3,14}	4.51	0.998
18 _{2,16} -18 _{3,15}	3.34	1.000

(c) METHYL CYANOFORMATE

5 ₂₃ -6 ₂₄	1.40	0.997
7 ₁₆ -7 ₂₅	5.41	1.024
8 ₁₇ -8 ₂₆	5.85	1.080
9 ₁₈ -9 ₂₇	5.71	1.019
10 ₁₉ -10 ₂₈	5.04	1.018
11 _{1,10} -11 _{2,9}	4.41	0.977
12 _{1,11} -12 _{2,10}	3.63	0.937
13 _{1,12} -13 _{2,11}	2.72	0.904
11 ₂₉ -11 ₃₈	11.06	1.048
12 _{2,10} -12 _{3,9}	11.59	1.028
13 _{2,11} -13 _{3,10}	11.23	1.025
14 _{2,12} -14 _{3,11}	10.27	1.031
15 _{2,13} -15 _{3,12}	8.89	1.045
16 _{2,14} -16 _{3,13}	7.63	1.012
17 _{2,15} -17 _{3,14}	5.89	1.012

TABLE 9.—Continued

(d) METHYL ACETATE

(i) $\text{CH}_3\text{COOCH}_3$

transition	obs. splittings ($A-E$) (MHz)	<u>predicted splittings</u> obs. splittings
$2_{02}-3_{13}$	2.5	1.005
$3_{03}-4_{14}$	2.25	1.043
$4_{04}-5_{15}$	1.74	1.195
$3_{13}-4_{04}$	-1.76	0.983
$4_{14}-5_{05}$	-1.5	0.814
$5_{15}-6_{06}$	small	—
$3_{12}-3_{21}$	3.9	1.058
$4_{13}-4_{22}$	5.50	1.018
$5_{14}-5_{23}$	5.49	1.000
$6_{15}-6_{24}$	4.79	1.018
$7_{16}-7_{25}$	4.08	0.974
$8_{17}-8_{26}$	3.18	0.975
$9_{18}-9_{27}$	2.45	0.942
$5_{05}-5_{14}$	2.40	0.996
$6_{06}-6_{15}$	2.68	0.974
$7_{07}-7_{16}$	3.17	1.009
$8_{08}-8_{17}$	4.32	0.991
$9_{27}-9_{36}$	8.76	1.004
$10_{28}-10_{37}$	7.13	0.998
$11_{29}-11_{38}$	5.12	1.005
$12_{39}-12_{48}$	14.08	1.003
$13_{3,10}-13_{49}$	11.89	1.005

(ii) $\text{CD}_3\text{COOCH}_3$

$3_{03}-4_{14}$	2.05	1.00
$3_{13}-4_{04}$	-1.22	1.446
$4_{14}-5_{05}$	-1.25	0.976
$4_{13}-4_{22}$	4.55	1.034
$5_{14}-5_{23}$	4.81	0.996
$6_{15}-6_{24}$	4.24	1.028
$7_{16}-7_{25}$	3.42	1.073
$8_{17}-8_{26}$	2.90	0.986
$6_{06}-6_{15}$	2.04	0.985

(iii) $\text{CD}_3\text{COOCD}_3$

$J_1(J-1)-J_2(J-2)$		
7	73.34	1.082
8	89.19	0.996
9	89.80	1.034
10	88.55	1.099
11	93.95	1.131
12	111.80	1.095
13	144.83	1.011
$J_0J-J_1(J-1)$		
6	92.24	0.905
7	115.89	0.878
8	122.00	1.027
9	147.28	1.046
10	195.30	0.955

TABLE 9.—Continued

(e) METHYL ACRYLATE

(i) $V = 0$

transition	obs. splittings ($A-E$) (MHz)	<u>predicted splittings</u> obs. splittings
1 ₀₁ -2 ₁₂	2.64	0.981
2 ₀₂ -3 ₁₃	2.40	1.000
3 ₀₃ -4 ₁₄	2.30	0.996
4 ₀₄ -5 ₁₅	2.18	1.018
4 ₁₄ -5 ₀₅	-2.16	0.979
5 ₁₅ -6 ₀₆	-1.89	0.979
6 ₁₆ -7 ₀₇	-1.70	0.982
7 ₀₇ -7 ₁₆	2.29	1.017
8 ₀₈ -8 ₁₇	2.29	1.031
9 ₀₉ -9 ₁₈	2.42	1.000
10 _{0,10} -10 _{1,9}	2.49	1.016

 $J_1(J-1)-J_2(J-2)$

5	3.33	0.982
6	4.75	0.983
7	5.21	0.990
8	5.38	0.976
9	5.17	0.992
10	4.93	0.994
11	4.61	0.996
12	4.23	1.000
13	3.81	1.008
14	3.43	1.003
15	3.01	1.020
16	2.73	1.011

 $J_2(J-2)-J_3(J-3)$

13	9.40	0.982
14	9.36	0.984
15	9.14	0.974
16	8.50	0.984
17	7.79	0.986

(ii) $V = 1$

3 ₀₃ -4 ₁₄	2.27	0.991
4 ₀₄ -5 ₁₅	2.13	1.019
5 ₁₅ -6 ₀₆	-1.81	1.000
6 ₁₆ -7 ₀₇	-1.70	0.947
7 ₀₇ -7 ₁₆	2.22	1.027
8 ₀₈ -8 ₁₇	2.14	1.084
7 ₁₆ -7 ₂₅	5.08	0.994
8 ₁₇ -8 ₂₆	5.16	0.994
10 ₁₉ -10 ₂₈	4.89	0.976
11 _{1,10} -11 ₂₉	4.43	1.011
12 _{1,11} -12 _{2,10}	4.04	1.022
13 _{1,12} -13 _{2,11}	3.76	0.997
14 _{1,13} -14 _{2,12}	3.12	1.077
15 _{1,14} -15 _{2,13}	2.79	1.075

The predicted splittings were obtained from the calculated barrier heights shown in table 10 using the parameters shown in table 8.

The value of 1190 cal/mol for methyl formate, which is included for comparison, was calculated by Curl¹ using $I_\alpha = 3.19$ a.m.u. \AA^2 . We have recalculated this value (in brackets) using the value $I_\alpha = 3.20$ a.m.u. \AA^2 which has been used for all the other compounds in table 10.

TABLE 10.— CH_3 (METHOXY) BARRIERS TO INTERNAL ROTATION

compound	barrier (cal/mol)
methyl fluoroformate ($\text{F}-\text{COOCH}_3$)	1077 ± 30
methyl propiolate ($\text{HC}\equiv\text{C}-\text{COOCH}_3$)	1266 ± 30
methyl cyanoformate ($\text{N}\equiv\text{C}-\text{COOCH}_3$)	1172 ± 30
methyl acetate ($\text{CH}_3-\text{COOCH}_3$)	1215 ± 30
($\text{CD}_3-\text{COOCH}_3$)	1208 ± 30
methyl acrylate ($\text{H}_2\text{C}=\text{CH}-\text{COOCH}_3$) $V = 0$	1220 ± 30
$V = 1$	1222 ± 30
methyl formate ($\text{H}-\text{COOCH}_3$)	1190 ± 40 ¹
	(1195)

Changes in the nature of the substituent result in small but real variations in the height of the methoxy barriers to internal rotation. It has been assumed that the only significant contribution to the latter is three-fold symmetric (i.e., V_3 only). No allowance has been made in the barrier calculations for any lack of rigidity in the molecules. Coupling between the methoxy torsion and other molecular vibrations would modify the internal rotation splittings and result in spurious values for the barrier heights. The vibrations most likely to couple with the methoxy torsions are other low-frequency modes of the same symmetry. These include (a) torsion about the central C—O bond in all esters, (b) torsion about the central C—C bond in methyl

TABLE 11.—FAR-INFRARED ABSORPTION BANDS CORRESPONDING TO THE TORSIONAL MODE ABOUT THE CENTRAL C—OCH₃ BAND IN SOME SUBSTITUTED FORMATES

compound	torsional frequency (cm ⁻¹)
methyl fluoroformate	190
methyl propiolate	171
methyl cyanoformate	181
methyl acetate ($\text{CH}_3\text{COOCH}_3$)	189
($\text{CD}_3\text{COOCH}_3$)	184
($\text{CD}_3\text{COOCD}_3$)	170
methyl acrylate	not available
methyl formate	328 ¹⁵

All substances were studied as liquids using an R.I.I.C. interferometer.

acrylate, and (c) torsion of the acetyl CH_3 group in methyl acetate. For methyl acrylate the barriers derived for the ground and for the first excited vibrational state of the C—C torsional mode are similar, strongly suggesting that coupling between this mode and the CH_3 torsion is small. That the coupling between the two methyl torsional vibrations in methyl acetate is small is suggested by the fact that the values derived for the methoxy barrier in $\text{CH}_3\text{COOCH}_3$ and $\text{CD}_3\text{COOCH}_3$ are almost identical, despite the fact that the acetyl torsional frequency is expected to change by a factor of approximately $\sqrt{2}$. The effect on the methoxy barrier height of the torsion of the OCH_3 group about the C—OCH₃ bond is less certain. Far infra-red spectra of liquid ester samples using an R.I.I.C. F720 interferometer show

absorptions between 170 and 190 cm^{-1} which are assigned to the torsional vibration about the $\text{C}-\text{OCH}_3$ bond¹⁴ (table 11). These absorptions are approximately 30-40 cm^{-1} higher than the methoxy torsional mode, and the mechanical coupling involved is probably small.

Although an unambiguous explanation of the trends in V_3 awaits accurate structural analysis of all the molecules, it is possible to rationalize the values in terms of simple chemical concepts provided it is assumed that the structural parameter most sensitive to substitution in the formate skeleton is the $\text{C}-\text{O}$ angle. This assumption

is reasonable since the electronegativity of the substituent would be expected to affect the electron distribution around both oxygen atoms, and the $\text{C}-\text{O}$ angle

is a sensitive function of the electron distribution around the ester oxygen. Altering the $\text{C}-\text{O}$ angle would in turn directly affect the distance of nearest approach of

the methyl hydrogens to the carbonyl oxygen, a factor which must figure strongly in the source of potential barrier opposing free internal rotation. In the extreme case

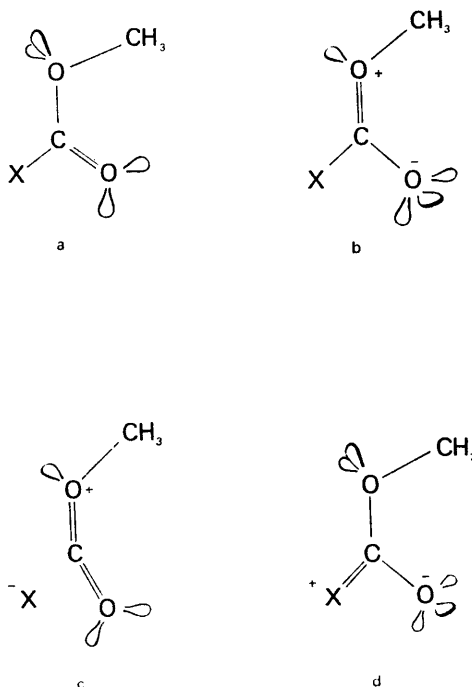


FIG. 6.—Canonical forms of the ester molecular skeleton. (a) depicts the usual ester molecular skeleton with the electron orbitals associated with the ether and carbonyl oxygen atoms distributed respectively in sp^3 and sp^2 hybrid systems. (b) represents the extreme resonance from which is generally regarded to be responsible for the planar structure of the heavy atoms in esters. This neglects any contributions from group X . (c) illustrates an extreme structure in which X is a very strong electron attracting group. The partial double bond character of the central $\text{C}-\text{O}$ bond is increased. (d) shows a structure in which X is a strong electron donating group. The carbonyl bond order decreases and the central $\text{C}-\text{O}$ bond remains essentially a single bond.

where the electrons of the ester oxygen atom arrange themselves in sp^2 hybrid orbitals the C—O angle is 120° , while on the other hand, an sp^3 distribution



would lead to a tetrahedral arrangement (fig. 6). Thus an electron-attracting substituent will strengthen both the C—O and C=O bonds, while an electron donating group will have the reverse effect. Support for this hypothesis is indicated from the observed relationship between the barrier heights and the corresponding carbonyl stretching frequencies

$$\begin{array}{l} \text{C=O stretch: } F > \text{CN} > \text{CH}_3 > \text{CH}_2\text{CH} > \text{H} > \text{HCC}, \\ V_3: \quad \quad \quad F < \text{CN} < \text{H} < \text{CH}_3 \simeq \text{CH}_2\text{CH} < \text{HCC}. \end{array}$$

With the exception of methyl formate, all the esters obey this inverse relationship.

The sum of the van der Waals radii for hydrogen and oxygen is 2.6 Å. For methyl formate,¹ Curl has shown that the distance of nearest approach of the methyl hydrogens to the carbonyl oxygen is 2.15 Å, while in the staggered equilibrium position it is 2.63 Å. If all other molecular parameters except the C—O



remain essentially unchanged on substitution, then an electropositive group should result in a closer distance of approach and consequently a higher barrier, and an electronegative group should have the reverse effect. This in fact is observed, the highest barrier occurring for methyl propiolate and the lowest for methyl fluoroformate. It is unlikely that the variation in the distance of nearest approach of the methyl hydrogens and the carbonyl oxygen atom need be large in order to explain the observed variations in barrier heights.

ACETYL CH_3 BARRIER

Barrier heights for some compounds of the type $\text{CH}_3\text{CO.X}$ are tabulated in table 12. For methyl acetate, internal rotation splittings attributable to the acetyl methyl top were identified only for the $\text{CD}_3\text{COOCD}_3$ isotopic species. These observed splittings (ranging from 70 to 200 MHz, table 9) would be much greater for $\text{CH}_3\text{COOCH}_3$ and $\text{CH}_3\text{COOCD}_3$, and were, in fact, too large to be recognized. The effect of the acetyl group was not observed on the spectrum of the $\text{CD}_3\text{COOCH}_3$ species even though it should be comparable to that seen in $\text{CD}_3\text{COOCD}_3$. In the former species, however, the presence of the methoxy CH_3 group further complicates the issue.

TABLE 12.— $\text{CH}_3(\text{ACETYL})$ BARRIERS TO INTERNAL ROTATION

compound	barrier (cal/mol)
acetone ($\text{CH}_3\text{—COCH}_3$)	778 ¹⁶
acetyl fluoride ($\text{CH}_3\text{—COF}$)	1041 ¹⁷
acetic acid ($\text{CH}_3\text{—COOH}$)	483 ⁵
methyl acetate ($\text{CD}_3\text{COOCH}_3$)	307 ± 50

The value of 307 cal/mol derived for the acetyl CH_3 barrier height is equivalent to a reduced barrier of 16 for $\text{CD}_3\text{COOCD}_3$, which is below the recommended lower limit of about 20 suggested by Woods for the “high barrier” approximations in his internal axis method.¹² The observed splittings, however, were measured in transitions of fairly high J and low K which represent the most favourable cases for these assumptions, and so the value of 307 ± 50 cal/mol is probably meaningful.

The barrier height is considerably lower than that found for acetic acid [483 cal/mol⁵]. One reason for the low values for both these compounds compared with others shown in table 12 is that the V_3 contribution to the barrier is decreased by the

site symmetry of the acetyl group—which in the extreme case of $\text{CH}_3-\text{C} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \diagdown \quad \diagup \\ \text{O} \end{array} -$ has

a six-fold potential barrier only. It is, however, surprising that the potential barrier in methyl acetate is lower than that found for acetic acid.

GENERAL DISCUSSION

All the barriers to internal rotation of the methoxy methyl group found for the five esters were close to the value calculated for methyl formate, showing that the introduction of various groups on the formyl carbon atom produces no “first order” effects on the internal freedom of the methyl group. The variations observed, however, although small and “second order”, are, we believe, real and in most instances fall well outside the uncertainties in the barriers. A complete analysis of these compounds relating the barrier heights to specific changes in molecular geometry will become possible only after studying many isotopic species for each. The application of newer microwave techniques such as double-resonance searching should however, facilitate analysis of several features remaining unsolved in the spectra of methyl acetate and methyl acrylate.

We are grateful to Dr. R. C. Woods for discussions in connection with his internal axis programme, to Prof. N. Sheppard, F.R.S., for the use of the R.I.I.C. interferometer, and to the Science Research Council for financial support. One of us (G. W.) acknowledges an S.R.C. studentship.

¹ R. F. Curl, *J. Chem. Phys.*, 1959, **30**, 1529.

² G. Williams, N. L. Owen and J. Sheridan, *Chem. Comm.*, 1968, 57.

³ H. G. Goswami and P. B. Sarker, *J. Indian Chem. Soc.*, 1933, **10**, 537.

⁴ W. Giuud, W. W. Nussler and K. Keller, *Patentschrift*, 1934, 592539.

⁵ W. J. Tabor, *J. Chem. Phys.*, 1957, **27**, 974.

⁶ C. C. Lin and J. D. Swalen, *Rev. Mod. Phys.*, 1959, **31**, 841.

⁷ J. S. Muentner, *J. Chem. Phys.*, 1968, **48**, 4544.

⁸ C. P. Smyth, *Dielectric Behaviour and Structure*, (McGraw Hill, New York, 1955).

⁹ K. Bolton, N. L. Owen and J. Sheridan, *Nature*, 1968, **218**, 266.

¹⁰ K. Bolton, *Ph.D. thesis* (University of Wales 1968).

¹¹ W. R. Fairheller and J. E. Katon, *J. Mol. Struct.*, 1968, **1**, 239, and private communication with G. W.

¹² R. C. Woods, *J. Mol. Spectr.*, 1967, **21**, 49.

¹³ D. R. Herschbach, *J. Chem. Phys.*, 1959, **31**, 91.

¹⁴ G. Williams and N. L. Owen, *Trans. Faraday Soc.*, 1971, **67**, 950.

¹⁵ T. Miyazawa, *Bull. Chem. Soc. Japan*, 1961, **34**, 691.

¹⁶ R. Nelson and L. Pierce, *J. Mol. Spectr.*, 1965, **18**, 344.

¹⁷ L. Pierce, C. Lawrence and L. C. Krisher, *J. Chem. Phys.*, 1959, **31**, 875.