769. *Molecular Polarisability: The Conformations of Some Simple Carboxylic Esters as Solutes.*

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The dipole moments, molar Kerr constants, etc., are recorded for methyl formate, chloroformate, acetate, propionate, isobutyrate, benzoate, and phthalate in benzene, for ethyl acetate in carbon tetrachloride, for dimethyl oxalate in dioxan, and for phenyl benzoate in benzene. Polarity and polarisability considerations indicate that in all cases the CO_2R group is non-planar, and that the assumption of a 30° rotation of the C–O–R triangle about the (CO)–O bond usually quantitatively reconciles *a priori* calculations with observations. Thus esters are probably conformationally similar as solutes and as gases.

During the last thirty years the stereo-structures of simple carboxylic esters have been investigated by many established physical methods, *e.g.*, dipole moments,[1-4] electron diffraction,[5,6] *X*-rays,[7] and microwave [8] and infrared absorption spectroscopy.[9,10] In general, the group CO·OR has been accepted as having the C=O and $O-C_{alkyl}$ bonds disposed in an *s-cis* relationship which is only slightly affected by temperature changes.[3] The methoxycarbonyl groups are stated [7] to be fully planar in crystalline dimethyl oxalate, but for gaseous methyl formate, chloroformate, and acetate deviations from the flat *cis*-conformations have been noted.[11,12] In terms of the rotation of the C–O–Alkyl triangle about the C–O bond, Smyth [13] has pointed out that with usual link moments and molecular geometry a departure of 30° still permits calculation of a molecular resultant of 1·8 D for methyl acetate, in satisfactory agreement with the value from experiment; by

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[1] Eucken and Meyer, *Phys. Z.*, 1929, **30**, 397.
[2] Zahn, *Phys. Z.*, 1932, **33**, 730.
[3] Marsden and Sutton, *J.*, 1936, 1383.
[4] Mizushima and Kubo, *Bull. Chem. Soc. Japan*, 1938, **13**, 174.
[5] O'Gorman, Shand, and Schomaker, *J. Amer. Chem. Soc.*, 1950, **72**, 4222.
[6] Ukaji, *Bull. Chem. Soc. Japan*, 1959, **32**, 1275.
[7] Dougill and Jeffry, *Acta Cryst.*, 1953, **6**, 831.
[8] Curl, *J. Chem. Phys.*, 1959, **30**, 1529.
[9] Walton and Hughes, *J. Amer. Chem. Soc.*, 1957, **79**, 3985.
[10] Josien, 19th Congr. groupe avance méthods anal. spectrog. prod. mét., 1956, p. 265.
[11] Allen and Sutton, *Acta Cryst.*, 1950, **3**, 46.
[12] Sutton *et al.*, " Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc. Spec. Publ.* No. 11, 1958.
[13] Smyth, " Dielectric Behaviour and Structure," McGraw-Hill, New York, 1955, p. 308.

TABLE 1.

Incremental values of Δn, Δn^2, Δd, $\Delta\varepsilon$, and ΔB for solutions in benzene at 25°.

Solute: Methyl chloroformate

$10^5 w_2$	$10^4\Delta n$	$10^4\Delta n^2$	$10^5\Delta d$	$10^4\Delta\varepsilon$	$10^{10}\Delta B$
870	−8	−25	207	545	48
1248	−12	−38	299	774	67
1877	−17	−53	447	1166	103
2014	—	—	—	1234	—
2180	−20	−63	521	1338	120
2853	—	—	—	—	158
3001	—	—	—	—	168
3006	—	—	—	—	170
3367	—	—	—	—	189
3600	−34	−106	864	2224	202
3756	—	—	—	2324	—
4659	—	—	—	—	269
4980	−46	−144	1184	3104	289
5210	—	—	—	—	304

whence $\Sigma\Delta n/\Sigma w_2 = -0{\cdot}093$; $\Sigma\Delta n^2/\Sigma w_2 = -0{\cdot}291$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}2387$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 6{\cdot}19$; $10^7\Delta B = 5{\cdot}27 w_2 + 10{\cdot}61 w_2^2$.

Solute: Methyl acetate

5436	−82	−246	180	2447	121
6436	−96	−288	212	2884	145
7500	−113	−339	237	3397	180
8604	−129	−386	277	3878	200
10,434	−155	−464	341	4688	218
11,513	−170	−509	378	5157	262

whence $\Sigma\Delta n/\Sigma w_2 = -0{\cdot}149$; $\Sigma\Delta n^2/\Sigma w_2 = -0{\cdot}447$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}0326$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 4{\cdot}50$; $\Sigma\Delta B/\Sigma w_2 = 2{\cdot}25_5 \times 10^{-7}$.

Solute: Methyl isobutyrate

1468	−20	−61	234	452	—
2874	−39	−118	283	882	34
4307	−57	−172	525	1326	49
5445	−74	−223	630	1677	53
6731	−90	−271	815	2062	76
7945	−105	−316	912	2426	93

whence $\Sigma\Delta n/\Sigma w_2 = -0{\cdot}134$; $\Sigma\Delta n^2/\Sigma w_2 = -0{\cdot}404$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}0118$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 3{\cdot}07$; $\Sigma\Delta B/\Sigma w_2 = 1{\cdot}12 \times 10^{-7}$.

Solute: Dimethyl phthalate

906	5	15	202	417	11
1245	7	21	319	561	17
1823	10	30	438	856	20
2116	11	33	459	961	25
2582	14	42	623	1136	34
2814	16	48	671	1282	37

whence $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}055$; $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}165$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}2361$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 4{\cdot}54$; $\Sigma\Delta B/\Sigma w_2 = 1{\cdot}25 \times 10^{-7}$.

Solute: Dimethyl oxalate. Solvent: Dioxan

384	—	—	58	216	8
534	—	—	80	319	10
782	—	—	135	434	17
1176	−1	−3	188	685	26
1502	—	—	230	843	31
1826	—	—	274	1013	36
2121	−2	−6	297	1198	45
2214	—	—	—	1273	49
3206	−3	−9	—	—	—
4490	−4	−12	—	—	—

whence $\Sigma\Delta n/\Sigma w_2 = -0{\cdot}009$; $\Sigma\Delta n^2/\Sigma w_2 = -0{\cdot}027$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}1520$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 5{\cdot}68$; $\Sigma\Delta B/\Sigma w_2 = 2{\cdot}11 \times 10^{-7}$.

Solute: Methyl formate

$10^5 w_2$	$10^4\Delta n$	$10^4\Delta n^2$	$10^5\Delta d$	$10^4\Delta\varepsilon$	$10^{10}\Delta B$
989	−17	−53	59	564	38
1645	−28	−88	87	872	61
2721	−42	−131	136	1442	98
3225	−55	−172	187	1741	122
3870	—	—	—	2063	151
4098	−65	−203	228	2176	156
4603	−78	−243	258	2530	179
5044	—	—	—	2688	192

whence $\Sigma\Delta n/\Sigma w_2 = -0{\cdot}165$; $\Sigma\Delta n^2/\Sigma w_2 = -0{\cdot}515$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}0553$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 5{\cdot}37$; $\Sigma\Delta B/\Sigma w_2 = 3{\cdot}81 \times 10^{-7}$.

Solute: Methyl propionate

1903	—	—	—	—	36
3001	—	—	—	—	56
3935	−51	−154	131	1440	69
4442	−58	−175	148	1543	80
6527	−83	−250	201	2268	118
8199	−103	−310	255	2837	146
9378	−119	−358	282	3213	—
11,734	−148	−444	377	4025	—

whence $\Sigma\Delta n/\Sigma w_2 = -0{\cdot}127$; $\Sigma\Delta n^2/\Sigma w_2 = -0{\cdot}382$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}0316$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 3{\cdot}47$; $\Sigma\Delta B/\Sigma w_2 = 1{\cdot}80_3 \times 10^{-7}$.

Solute: Methyl benzoate

1024	—	—	—	—	31
1611	—	—	—	—	56
2476	2	6	418	696	87
3114	—	—	542	850	118
4068	3	9	708	1134	140
5111	—	—	910	1438	185
6274	5	15	1039	1737	236
6875	—	—	1210	1918	251
9899	8	24	—	—	—
13,242	10	30	—	—	—
16,875	14	42	—	—	—
19,006	15	45	—	—	—

whence $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}008$; $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}024$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}1729$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 2{\cdot}78$; $\Sigma\Delta B/\Sigma w_2 = 3{\cdot}61 \times 10^{-7}$.

Solute: Phenyl benzoate

2026	11	33	418	448	45
3049	17	51	647	671	77
4105	22	66	857	889	88
5254	28	84	1109	1140	94
6555	36	108	1360	1442	145
7634	40	120	1603	1670	164

whence $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}054$; $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}162$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}2094$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 2{\cdot}19$; $\Sigma\Delta B/\Sigma w_2 = 2{\cdot}14 \times 10^{-7}$.

Solute: Ethyl acetate. Solvent: Carbon tetrachloride

2700	−43	−126	−3279	1875	62
4219	−64	−188	−5052	2939	94
6225	−93	−279	−7344	4273	136
7811	−119	−348	−9098	5289	181
11,094	−163	−476	−12,581	7339	229
12,599	−182	−531	−14,136	8973	300

whence $\Delta n = -0{\cdot}158 w_2 + 0{\cdot}128 w_2^2$; $\Delta n^2 = -0{\cdot}472 w_2 + 0{\cdot}450 w_2^2$; $\Delta d = -1{\cdot}2345 w_2 + 0{\cdot}0902 w_2^2$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 6{\cdot}87$; $\Sigma\Delta B/\Sigma w_2 = 2{\cdot}24 \times 10^{-7}$.

electron diffraction[11,12] this angle has been estimated as 25° in methyl acetate and formate, and as 20° in methyl chloroformate (with limits for the averages of 0—35°, 0—40°, and 0—30°, respectively). The dipole moments of esters as vapours and as solutes in benzene are almost the same (cf. p. 304 of ref. 13), and similarities of conformation in the two states seem thereby indicated; however, Smyth's discussion[13] suggests that polarity might be too insensitive a property from which properly to draw such a conclusion. By contrast, measurements[14] dependent on the anisotropy of molecular polarisability are very suitable for the purpose, as many examples[15] have shown. Accordingly we have examined the molar Kerr constants, dielectric polarisations, etc., at infinite dilution in non-polar media, of the ten esters listed in the Tables below. Of these, the first three present only the problem mentioned above; the remainder, having further possibilities of rotational isomerism, raise additional questions. Certain esters (azodiformates, maleates, fumarates, etc.,[16] vinyl acetate,[17] the mono- and di-acetoxy- and -ethoxycarbonyl-benzenes[18]) have previously been studied in these laboratories; except with vinyl acetate, the CO_2R groups were regarded as approximately planar. In the light of present results some of the earlier conclusions require amendment in minor details.

EXPERIMENTAL

Materials.—Commercial samples of the esters were purified as described elsewhere;[19] methyl isobutyrate was prepared by Vogel's procedure.[20] The m. p.s or b. p.s of the specimens used as solutes conformed to those cited in refs. 19 and 21—24. Benzene and carbon tetrachloride, as solvents, were given the standard pretreatment noted in ref. 25, p. 45; the dioxan was as used by Le Fèvre and Sundaram.[26]

Measurements and Results.—These are listed in Tables 1—3. Table 1 shows, for solutions each containing weight fractions w_2 of solute in the solvent named, the differences, Δn, Δn^2

TABLE 2.

Total polarisations at infinite dilution, molecular refractions, and dipole moments calculated from Table 1.

Solute	M_2	$\alpha\varepsilon_1$	β	$\gamma^1 n_1^2$	$_\infty P_2$ (c.c.)	R_D obs. (c.c.)	μ *
$H\cdot CO_2Me$	60·1	5·37	0·0633	−0·515	79·76	12·94	1·80
$Cl\cdot CO_2Me$	94·5	6·19	0·2732	−0·291	133·44	17·77	2·37
$Me\cdot CO_2Me$	74·1	4·50	0·0373	−0·447	86·88	17·56	1·83
$Et\cdot CO_2Me$	88·1	3·47	0·0361	−0·382	86·28	22·00	$1·75_7$
$Me_2CH\cdot CO_2Me$ ...	102·1	3·07	0·0135	−0·404	93·21	25·88	1·80
$Ph\cdot CO_2Me$	136·2	2·78	0·1979	0·024	108·42	37·21	1·84
o-$C_6H_4(CO_2Me)_2$	194·2	4·54	0·2702	0·165	213·92	53·55	2·78
$Ph\cdot CO_2Ph$	198·2	2·19	0·2396	0·162	133·03	56·63	1·90
$Me\cdot CO_2Et$ †	88·1	6·87	−0·7791	−0·472	92·77	22·31	1·84
$(CO_2Me)_2$ ‡	118·1	5·68	0·1479	−0·027	138·61	24·20	2·35

* Calc. by assuming $_DP = 1·05R_D$ observed. Solvent: † CCl_4; ‡ dioxan; in other cases, benzene.

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[14] Le Fèvre and Le Fèvre, (*a*) *J.*, 1953, 4041; (*b*) *Rev. Pure Appl. Chem.* (*Australia*), 1955, **5**, 261; (*c*) Chap. XXXVI in " Physical Methods of Organic Chemistry," ed. Weissberger, Interscience Publ., Inc., New York, 3rd edn., Vol. I, p. 2459.

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[20] Vogel, " Practical Organic Chemistry," Longmans, London, 3rd edn., 1956.

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[23] Beilstein's " Handbuch der organischen Chemie."

[24] Huntress and Mulliken, " Identification of Pure Organic Compounds," John Wiley, New York, 1941.

[25] Le Fèvre, " Dipole Moments," Methuen, London, 3rd edn., 1953.

[26] Le Fèvre and Sundaram, *J.*, 1962, 1494.

TABLE 3.

Molar Kerr constants at infinite dilution calculated from Tables 1 and 2.

Solute	γ	δ	$10^{12}{}_{\infty}({}_{m}K_{2})$	Solute	γ	δ	$10^{12}{}_{\infty}({}_{m}K_{2})$,
$H{\cdot}CO_2Me$	−0·110	9·29	35·57	$Ph{\cdot}CO_2Me$	0·005	8·80	85·38
$Cl{\cdot}CO_2Me$	−0·062	12·85	76·80	o-$C_6H_4(CO_2Me)_2$	0·037	3·05	23·67
$Me{\cdot}CO_2Me$	−0·100	5·50	25·00	$Ph{\cdot}CO_2Ph$.........	0·036	5·22	73·65
$Et{\cdot}CO_2Me$	−0·085	4·40	25·54	$Me{\cdot}CO_2Et$ *	0·109	32·00	20·07
$Me_2CH{\cdot}CO_2Me$ ...	−0·089	2·73	18·37	$(CO_2Me)_2$ †	−0·006	31·03	40·06

Solvent: * CCl_4; † dioxan; in other cases benzene.

Δd, $\Delta\varepsilon$, and ΔB between the refractive indexes, the squares of the refractive indexes, the densities, the dielectric constants, and the Kerr effects, respectively, of the solutions and the solvent. For the pure solvents (*i.e.*, when $w_2 = 0$), the physical properties named have the values given in refs. 14*b* or *c*, and 26. All measurements were at 25°. Polarisations, dipole moments, molar Kerr constants, etc., deduced from Table 1 follow as Tables 2 and 3. Definitions of symbols and explanations of the calculations employed are in refs. 14*b* and *c*; a brief summary is also in ref. 26.

DISCUSSION

Previous Measurements.—Dipole moments for six of the ten substances listed in Table 2 have been reported previously. The literature since 1948 contains values given in Table 4. Measurements reported before 1948 are listed by Wesson;[31] they comprise only methyl chloroformate, methyl acetate, methyl propionate, methyl benzoate, phenyl benzoate, and ethyl acetate in various solvents and at various temperatures. The values given differ considerably among themselves; their ranges are noted in Table 5. Wesson's tables contain no entry for methyl formate, methyl isobutyrate, dimethyl phthalate, or dimethyl oxalate. In several instances the moments given in Table 2 disagree with those in Tables 4 and 5, probably because of the paucity of solutions examined during these earlier determinations; it is not that different approximations for distortion polarisations have been made. Curl's estimate[8] of $\mu = 1{\cdot}77$ D from microwave studies of methyl formate compares satisfactorily with that now obtained (1·80 D) by the dielectric-constant method; the same is not true for the microwave results for methyl acetate (1·58 D) or benzoate (1·69 D). Although strictly not relevant, the electric birefringences, relatively to carbon disulphide, for ethyl acetate and methyl benzoate as pure liquids are quoted in Vol. VII of ref. 22.

TABLE 4.

Dipole moments published since 1948.

Solute	Solvent	μ (D)	Ref.	Solute	Solvent	μ (D)	Ref.
$Me{\cdot}CO_2Me$	C_6H_6	1·45	27	$Et{\cdot}CO_2Me$	C_6H_6	1·73	30
,,	,,	1·61	28	,,	1,4-Dioxan	1·72	,,
$Ph{\cdot}CO_2Me$	,,	1·70	27	,,	Toluene	1·64	,,
$Me{\cdot}CO_2Et$	CCl_4	1·81	29	,,	$CHCl_3$	$1{\cdot}40_7$	,,
				,,	BuOAc	$0{\cdot}58_3$	,,

TABLE 5.

Dipole moments (D) published before 1948.

$Cl{\cdot}CO_2Me$ 2·22; $Me{\cdot}CO_2Me$ 1·67—2·2; $Et{\cdot}CO_2Me$ $1{\cdot}65_7$—$1{\cdot}73_5$; $Ph{\cdot}CO_2Me$ 1·80—2·52; $Ph{\cdot}CO_2Ph$ 1·80—1·92; $Me{\cdot}CO_2Et$ 1·74—2·00.

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[27] Jatkar and Phansalkar, *J. Univ. Poona Sci. Technol.*, 1953, **4**, 45.

[28] Gopala Krishnan, *Trans. Faraday Soc.*, 1957, **53**, 767.

[29] Kapustin, *J. Exp. Theor. Phys.* (*U.S.S.R.*), 1947, **17**, 30.

[30] Marchal and Lapp, *J. Polymer Sci.*, 1958, **27**, 571.

[31] Wesson, " Tables of Electric Dipole Moments," Technology Press, Massachusetts Inst. Technology, 1948.

Dipole Moments and Conformations.—The moments listed in Table 2 are consistent with a general non-planarity of the group CO·OR: let inter-bond angles be taken as in Sutton's tables,[12] polarity components [31,32] of $2{\cdot}8_0$ D and $1{\cdot}2_8$ D be attributed to the C=O link and the C–O–C triangle, respectively, and the moments of H–C bonds be regarded as negligibly small; the observed resultants, *via* the usual equation, $\mu^2_{\text{resultant}} = (2{\cdot}80)^2 + (1{\cdot}28)^2 + 2 \times 1{\cdot}28 \times 2{\cdot}80 \cos \theta$, show the two components to interact in all cases within the range 147—153° (Table 6). The direction of action of $\mu_{\text{resultant}}$ in the space formula of any of the esters then follows from the relation: $\tan \alpha = 1{\cdot}28 \sin \theta/(2{\cdot}8 + 1{\cdot}28 \cos \theta)$, where α is the angle between $\mu_{\text{resultant}}$ and $\mu_{\text{C=O}}$. (With ethyl acetate, for which the solvent is carbon tetrachloride, 1·32 D, *i.e.*, $\mu_{\text{Me}_2\text{O}}$ in this medium,[32] has been used instead of $1{\cdot}2_8$ D, the apparent moment of Me_2O in benzene.) The values of θ and α so obtained are of interest for their near-constancy, suggesting no great difference in the non-planarities of CO_2R from ester to ester; they are roughly those expected if the C–O–R triangle is raised out of the flat configuration by a rotation of *ca.* 30° about the C–O bond, *i.e.*, if the conformations of esters as solutes resemble those described in refs. 11—13 for esters as gases.

TABLE 6.

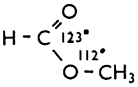
Angles of interaction between $\mu_{\text{C·O·C}}$, $\mu_{\text{C=O}}$, and $\mu_{\text{resultant}}$.

Ester	Angle θ between $\mu_{\text{C·O·C}}$ and $\mu_{\text{C=O}}$	Angle α between $\mu_{\text{C=O}}$ and $\mu_{\text{resultant}}$	Ester	Angle θ between $\mu_{\text{C·O·C}}$ and $\mu_{\text{C=O}}$	Angle α between $\mu_{\text{C=O}}$ and $\mu_{\text{resultant}}$
H·CO·OMe...	150·5°	20·5°	Et·CO·OMe	153·0°	19·3°
Me·CO·OMe	148·8	21·1	Me_2CH·CO·OMe	150·5	20·5
Me·CO·OEt	147·0	22·6	Ph·CO·OMe	148·2	21·5

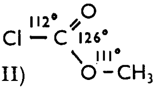
Molar Kerr Constants and Conformations.—This subject is approached generally as follows: The principal axes of polarisability b_1, b_2, and b_3 are calculated (by the method outlined on p. 2486 of ref. 14*c* or p. 3 of ref. 15, and fully described in ref. 33) for alternative conformations, from the known [12] geometrical specifications of such structures and the accepted longitudinal, transverse, and "vertical" polarisabilities (b_{L}^{XY}, b_{T}^{XY}, and b^{XY}) of the various bonds X–Y. The values of the last [14*b*-*d*,15] are:

	b_{L}	b_{T}	b_{V}
C–H	0·064	0·064	0·064
C–O	0·081	0·039	0·039
C=O	0·230	0·140	0·046

(Here, and elsewhere, polarisabilities b_i are quoted as 10^{-23} c.c. units.) In conjunction with estimates of the directions of action of the molecular resultant dipole moments, the molar Kerr constants are then deduced (from the equations given, *e.g.*, on p. 2480 of ref. 14*c* or p. 2 of ref. 15) for the models under consideration and compared with the $_\infty({}_{\text{m}}K_2)$'s observed.



(I)



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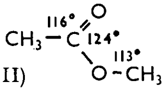

(III)

Methyl formate, chloroformate, and acetate are simple cases in which rotational isomers can only be due to the relative orientations of the C=O and OMe groups. Four forms are therefore investigated: A and B, both planar, in which the O–Me and carbonyl bonds lie, respectively, *cis* and *trans* to one another, C in which the C–O–Me triangle has been rotated (about the C–O line) 90° above the plane containing it in A, and D as C but after a rotation of 30°. Inter-bond angles are taken in all conformations to be as shown in (I)—(III) for the *cis*-flat structures (cf. ref. 12). The mutually perpendicular axes

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[32] Aroney, Le Fèvre, and Saxby, *J.*, 1962, 2886.
[33] Eckert and Le Fèvre, *J.*, 1962, 1081.

X, *Y*, and *Z* (used to define the locations of b_1, b_2, and b_3 and μ_1, μ_2, and μ_3) are chosen so that C=O is parallel to *X*, and *Y* is at 90° to *X* in the O=C–O plane.

Results of calculations are summarised in Table 7. With methyl chloroformate the *trans*-conformation has not been considered since its existence appears most improbable from the magnitude of μ observed. The two computations, A and A′, for this ester differ in that, with A, the polarisabilities of C–Cl are as in methyl chloride[15] while with A′ they are as in chloroform, vinylidene dichloride, etc. Since the ${}_{\rm m}K$'s calc. on the methyl chloride basis for conformations of type A, C, or D are all less than that observed, the alternative values ($b_{\rm L}^{\rm CCl} = 0{\cdot}399$, $b_{\rm T}^{\rm CCl} = b_{\rm V}^{\rm CCl} = 0{\cdot}185$) are evidently more appropriate and have been used.

TABLE 7.

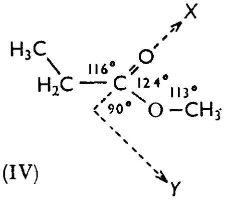
Polarisability semi-axes, moment components, etc., for methyl formate, chloroformate, and acetate.

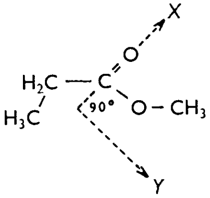
Conformation type	Principal semi-axes *	Direction cosines with			Dipole moment components (D) *	$10^{12}{}_{\rm m}K$ calc.
		X	*Y*	*Z*		
			Methyl formate			
A	0·589$_5$	1	0	0	1·80	49·45
	0·532$_5$	0	1	0	0	
	0·380$_0$	0	0	1	0	
B	0·617$_5$	1	0	0	1·80	64·8
	0·504$_4$	0	1	0	0	
	0·380$_0$	0	0	1	0	
C	0·580$_8$	0·9834	−0·1796	0·0251	1·16	−1·72
	0·510$_0$	0·1735	0·9213	0·3480	0·67	
	0·411$_4$	−0·0529	−0·3448	0·9372	−1·20	
D	0·587$_2$	0·9966	−0·0693	0·0448	1·65	30·8
	0·526$_7$	0·0637	0·9912	0·1161	0·033	
	0·388$_3$	−0·0524	−0·1128	0·9922	−0·723	
			Methyl chloroformate			
A	0·727	0·7278	−0·6858	0	2·11	52·9
	0·807	0·6858	0·7278	0	−1·08	
	0·536	0	0	1	0	
A′	0·700	0·8790	−0·4772	0	1·775	84·7
	0·878	0·4772	0·8790	0	−1·570	
	0·501	0	0	1	0	
D	0·702	0·8780	−0·4787	0·0072	1·75	75·5
	0·866	0·4777	0·8770	0·0512	−1·56	
	0·511	−0·0308	−0·0415	0·9987	−0·344	
			Methyl acetate			
A	0·781	0·7840	0·6205	0	1·43$_5$	46·3
	0·724	0·6205	−0·7840	0	−1·13$_6$	
	0·535	0	0	1	0	
B	0·787	0·9986	0·0523	0	1·82$_7$	62·0
	0·718	0·0523	−0·9986	0	−0·09$_6$	
	0·535	0	0	1	0	
C	0·766	0·7889	0·6000	0·1327	1·18	−8·62
	0·716	−0·6016	0·7891	0·1237	0·60	
	0·558	−0·1253	−0·1312	0·9834	−1·26$_5$	
D †	0·773	0·8767	0·4752	0·0744	1·34$_2$	25·9$_5$
	0·722	−0·4737	0·8799	−0·0376	1·02$_4$	
	0·544	−0·0833	−0·0023	0·9965	−0·70$_4$	

* Polarisability semi-axes and dipole moment components listed in descending orders as b_1, b_2, and b_3, and μ_1, μ_2, and μ_3. † *X* and *Y* in the plane of the acetyl group, *X* parallel to the C–C link.

Comparisons between the ${}_{\rm m}K$'s predicted (Table 7) and those observed (Table 3) show that for each ester an " effective " conformation of type D provides near-agreement with experiment. Small variations of the angle between 30° and 25° could improve the concordance, but in view of the assumptions underlying the calculations the point is not stressed; we consider it satisfactory that we estimate the non-planarity of methyl formate and acetate as within the limits given by electron diffraction,[11] and only 10° different from that (20°) reported [12] for methyl chloroformate by the same method.

Methyl propionate presents the additional problem of the conformation of its CH_3–CH_2 bond, so that theoretically four flat extreme forms should be considered. However, the two having C=O and O–CH_3 mutually *trans* can be eliminated on polarity grounds, leaving structures (IV) and (V); in Table 8 these are designated A and A′, respectively, while D


(IV)


(V)

indicates structure (IV) in which the methyl group is raised above the O=C–O plane by the 30° rotation already prescribed for (I)—(III). Again, a conformation of type D appears satisfactory, ${}_{m}K$ calc. being $27{\cdot}1 \times 10^{-12}$, and ${}_{m}K$ observed $25{\cdot}5 \times 10^{-12}$.

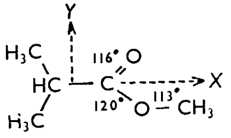
TABLE 8.

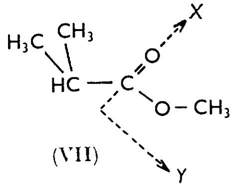
Polarisability semi-axes, moment components, etc., for three conformations of methyl proprionate.

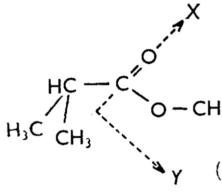
Conformation type	Principal semi-axes *	Direction cosines † with X	Y	Z	Dipole moment components (D) *	$10^{12}{}_{m}K$ calc.
A	$0{\cdot}948_5$	1	0	0	$1{\cdot}75_7$	$48{\cdot}9_5$
	$0{\cdot}937_7$	0	1	0	0	
	$0{\cdot}690_8$	0	0	1	0	
A′	0·9849	0·9981	0·0610	0	$1{\cdot}75_4$	67·7
	$0{\cdot}901_3$	0·0610	−0·9981	0	$-0{\cdot}10_7$	
	$0{\cdot}690_8$	0	0	1	0	
D	$0{\cdot}952_3$	0·8732	−0·4873	0·0047	$1{\cdot}42_6$	27·1
	$0{\cdot}924_7$	0·4853	0·8706	0·0812	$0{\cdot}74_2$	
	$0{\cdot}700_0$	−0·0437	−0·0686	0·9967	$-0{\cdot}71_0$	

* Cf. footnotes to Table 7. † X and Y axes shown on (IV) and (V).

With methyl isobutyrate, in which the CO·OMe group has internally a *cis*-arrangement, three extreme forms are possible, one (VI) in which the Me · · · Me line is parallel to the plane of the O=C–O triangle, and two (VII) and (VIII) in which it is perpendicular to it.


(VI)


(VII)


(VIII)

For identification in Table 9, forms with the *cis*-planar arrangement of CO·OMe are designated type A, and forms in which the O–Me has undergone a 30° rotation are shown as type D with an indication of the flat form (*i.e.*, either VI, VII, and VIII) from which they are generated.

It is seen that the ${}_{m}K$'s calc. for (VI)—(VIII), in which the CO·OMe groups are planar, all exceed the ${}_{m}K$ observed. Twisting the C–O–Me plane in (VIII) about the C–O bond by 30° leads to an ${}_{m}K$ calc. in good agreement with that found; twisting that in (VII) by *ca.* 20° does the same. However, because models suggest steric hindrances between the

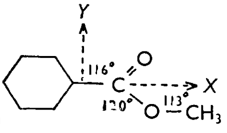
TABLE 9.

Semi-axes, component moments, etc., calc. for methyl *iso*butyrate.

Conformation types	Principal semi-axes *	Direction cosines † with *X*	*Y*	*Z*	Dipole moment components (D) *	$10^{12}{}_{\mathrm{m}}K$ calc.
A(VI)	1·094	0·9976	−0·0698	0	1·01	44·6
	1·127	0·0698	0·9976	0	1·49	
	0·893	0	0	1	0	
D(VI)	1·077	0·9113	−0·4079	−0·0568	0·22	38·2
	1·133	0·4081	0·9129	−0·0087	1·67	
	0·903	0·0554	−0·0153	0·9984	−0·62	
A(VII)	1·085	1	0	0	1·80	26·3
	1·087	0	1	0	0	
	0·942	0	0	1	0	
D(VII)	1·085	0·8127	0·6586	0·1270	1·29	12·7$_5$
	1·081	−0·5780	0·8143	0·0529	1·01	
	0·948	−0·0733	−0·1164	0·9905	0·75	
A(VIII)	1·124	0·9397	0·3420	0	1·69	37·0$_5$
	1·048	0·3420	−0·9397	0	0·62	
	0·942	0	0	1	0	
D(VIII)	1·119	0·8055	0·5890	0·0648	1·31	18·7
	1·047	−0·5916	0·8056	0·0315	−1·02	
	0·948	−0·0336	−0·0637	0·9974	−0·69	

* See footnotes to Table 7. † Directions of *X*, *Y*, and *Z* are indicated in (VI)—(VIII).

methyl groups and the ketonic oxygen in (VII), and because 30° seems a generally satisfactory angle in esters, we prefer form D (VIII) as a representation of the effective conformation of methyl isobutyrate. We cannot eliminate the possibility of the solute's being a mixture of forms, *e.g.*, of (VI)D and (VIII)D, which in suitable proportions could also produce an ${}_{\mathrm{m}}K$ of $18{\cdot}4 \times 10^{-12}$; at the same time, we know of no evidence against this dissolved substance's being a single form.



(IX)

The magnitude of the dipole moment of methyl benzoate suggests that the C=O and Me–O bonds are disposed in a *cis*-manner; diagram (IX) represents the fully flat conformation, and defines the directions of the *X* and *Y* axes; in Table 10 this form is cited as A(IX), and its modification produced by rotation the C–O–Me plane around C–O by 30° is cited as D(IX). We assume that, through resonance, the C=O bond is coplanar with the phenyl ring, in which case D(IX) appears as the "effective" conformation (${}_{\mathrm{m}}K$ calc. $89{\cdot}5 \times 10^{-12}$, observed $85{\cdot}4 \times 10^{-12}$).

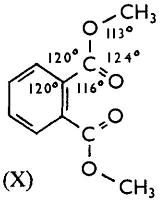
TABLE 10.

Semi-axes, component moments, etc., for methyl benzoate.

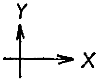
Conformation types	Principal semi-axes	Direction cosines with * *X*	*Y*	*Z*	Dipole moment components (D)	$10^{12}{}_{\mathrm{m}}K$ calc.
A(IX)	1·634	1	0	0	1·81	124·5
	1·598	0	1	0	1·65	
	1·014	0	0	1	0	
D(IX)	1·636	0·8746	0·4841	0·0276	1·40	89·5
	1·586	−0·4839	0·8750	−0·0122	1·00	
	1·023	−0·0300	−0·0028	0·9995	−0·66	

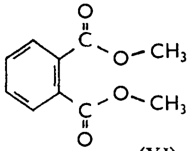
* See footnotes to previous Tables.

With dimethyl phthalate the problems are multiplied. Scale models indicate that a completely planar form is sterically impossible. In addition, $10^{12}{}_{\mathrm{m}}K$ calc. for (X) is 472, and for (XI) is 33·5, which both exceed 23·7 as measured, and the moment observed (2·78 D) is much higher than would be expected for (XI). Models suggest the feasibility of structures (XII) and (XIII) (not illustrated) in which the two CO_2Me groups are twisted in opposite or the same directions, respectively, so that their planes are perpendicular to the Ar ring; (XII) would agree with μ_{observed} but corresponds to an ${}_{\text{m}}K$ of $65{\cdot}1 \times 10^{-12}$, while (XIII) requires a dipole moment larger than that measured and leads to an algebraically negative ${}_{\text{m}}K$ ($-26{\cdot}7_5 \times 10^{-12}$). Although either (XII) or (XIII) alone is unsatisfactory, their coexistence in a mixture could account for the experimental observations. We add, however, that a single conformation (XIV, not illustrated) can be devised, which is satisfactory (although not unique); it is generated from a model in which one CO_2 triangle (*a*) is in the plane of the C_6H_4 ring and the other CO_2 (*b*) perpendicular to it; (*a*) and (*b*) are twisted about their C_{Ar}–C bonds (looking from C_{Ar} to the $C_{C=O}$) respectively 15° and 5° clockwise; both methoxycarbonyl groups are made non-planar by 30° rotation (also clockwise, looking from C to O) about their C–O bonds. The calculated ${}_{\text{m}}K$ (Table 11) is then $25{\cdot}7 \times 10^{-12}$ (observed, $23{\cdot}7 \times 10^{-12}$).



(X)





(XI)

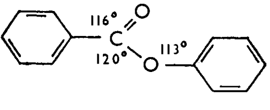
TABLE 11.

Semi-axes, component moments, etc., for dimethyl phthalate.

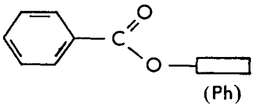
Conformation	Principal semi-axes	Direction cosines with * *X*	*Y*	*Z*	Dipole moment components	$10^{12}\,{}_{\text{m}}K$ calc.
(X)	2·253	1	0	0	2·52	471·8
	1·971	0	1	0	0	
	1·294	0	0	1	0	
(XI)	2·091	1	0	0	0·2	35·2
	2·133	0	1	0	0	
	1·294	0	0	1	0	
(XII) †	1·970	1	0	0	1·41	65·1
	1·776	0	1	0	0	
	1·772	0	0	1	0	
(XIII) †	1·972	0·9951	0	0·0993	1·52	$-26{\cdot}7_5$
	1·776	0	1	0	0	
	1·770	−0·0993	0	0·9951	2·63	
(XIV) †	2·067	0·9961	0·0332	0·0818	0·89	25·7
	1·928	−0·0329	0·9993	0·0180	2·28	
	1·523	−0·0820	−0·0175	0·9965	1·33	

* *X* and *Y* in the C_6H_4 plane, with *Y* passing through the carbons *ortho* to each CO_2Me group.
† For explanation of these conformations see the cursive text.

Table 12 summarises calculations for three conformations of phenyl benzoate, (XV) which is flat, (XVI) in which the phenoxyphenyl is perpendicular to the plane of (XV), and (XVII) (not illustrated) produced by a 70° rotation of the phenoxyphenyl group.



(XV)



(XVI)

As with methyl benzoate, we consider the benzoyl group to be planar through conjugation. A conformation such as (XVII) appears adequate (${}_{\text{m}}K$ calc. $\mathbf{76{\cdot}4_5} \times 10^{-12}$; obs. $\mathbf{73{\cdot}6_5} \times$

10^{-12}), although others (not examined) in which the phenoxy-group is lifted from the benzoyl plane and the phenyl ring twisted less than 70° might also satisfy the requirements.

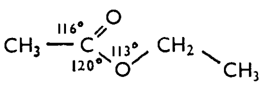
Dipole-moment measurements on ethyl acetate favour a *cis*- rather than a *trans*-arrangement of the C=O and Et–O bonds, but give no guide to the internal conformation of the ethyl group. Extreme planar forms of the *s-cis*-molecule are (XVIII) and (XIX); from these, non-planar variants can be derived in two ways: (*a*) by keeping the Me–CO·O·C flat and rotating the C–CH_3 around a cone, or (*b*) by keeping the Me·CO·O flat and rotating both the O–CH_2 and CH_2–CH_3 units as two different cones. The process (*b*) involves complicated polarisability calculations, the difficulties of which are, however, reduced if in ethyl acetate the skeletal conformation of methyl acetate (see above) is retained and a (*b*)-type non-planar version of (XVIII) thus created. We note that Karpovich,[34] from acoustic relaxation measurements, concluded that rotations about C–O occur in this ester, but he did not propose any particular angle. We suggest therefore that the extra C–C linkage be added to methyl acetate so that it lies approximately parallel to the Ac–O bond in a plane which itself is parallel to that containing Me·CO·O. Scale models indicate that rotations of CH_2–CH_3, about the O–CH_2 axis, by more than *ca.* ±30° from this position are unlikely because of interactions between the carbonyl-oxygen and the methylene-hydrogen atoms. Table 13 contains the relevant calculations;

TABLE 12.

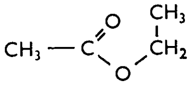
Semi-axes, component moments, etc., for phenyl benzoate.

Conformation	Principal semi-axes	Direction cosines with * X	Y	Z	Dipole moment components	$10^{12}{}_{m}K$ calc.
(XV)	2·499	1	0	0	0·83	239·0
	2·462	0	1	0	1·71	
	1·493	0	0	1	0	
(XVI)	2·503	0·9871	−0·1599	0	0·55	−10·2
	2·072	0·1599	0·9871	0	1·82	
	1·878	0	0	1	0	
(XVII) †	2·504	0·9856	0·1689	0·0087	1·11	$76{\cdot}4_5$
	2·163	−0·1611	0·9222	0·3514	1·44	
	1·787	0·0513	−0·3478	0·9362	−0·554	

* *X* and *Y* in the plane of the benzoyl group, *X* being parallel to the C_6H_5–C bond. † For conformation (XVII) see cursive text.



(XVIII)



(XIX)

TABLE 13.

Semi-axes, component moments, etc., for ethyl acetate.

Conformation	Principal semi-axes	Direction cosines with * X	Y	Z	Dipole moment components	$10^{12}{}_{m}K$ calc.
(XVIII)	0·940	1	0	0	1·84	47·1
	0·946	0	1	0	0	
	0·691	0	0	1	0	
(XIX)	0·982	1	0	0	1·84	72·4
	0·904	0	1	0	0	
	0·691	0	0	1	0	
(XVIII*b*)	0·928	0·8300	0·5531	0·0715	1·43	24·1
	0·949	−0·5523	0·8330	−0·0328	0·895	
	0·699	−0·0777	−0·0122	0·9969	−0·735	

* *X* and *Y* in the Me·CO_2 plane, with *X* parallel to the C=O bond.

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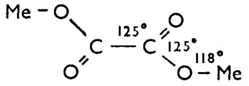
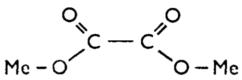
[34] Karpovich, *J. Chem. Phys.*, 1953, **21**, 1120; 1954, **22**, 1767.

the (*b*)-type modification of (XVIII) leads to an $_{m}K$ ($24{\cdot}1 \times 10^{-12}$) close to that observed ($20{\cdot}1 \times 10^{-12}$).

Literature references to the nature of dimethyl oxalate suggest that in the crystal this molecule adopts a *trans*-conformation [7,35] whereas in the liquid or gaseous state *cis*- and *trans*-forms coexist.[36] Owing to its negligible solubility in benzene our measurements were made with dioxan as solvent, the dipole moment and the molar Kerr constant found being $2{\cdot}3_5$ D and $40{\cdot}1 \times 10^{-12}$, respectively. Corresponding values determined earlier [16] for diethyl oxalate in carbon tetrachloride are $2{\cdot}4_1$ D and $45{\cdot}4 \times 10^{-12}$. The non-zero magnitudes of these moments show, of course, that neither ester as a solute exists alone as a flat *trans*-arrangement. Table 14 presents calculations for the following forms: flat *trans* (XX), flat *cis* (XXI), and two non-planar variants of the last, *viz.*, (XXII) and (XXIII); in (XXII) the CO_2Me groups are each flat but their planes are twisted in opposite senses about the central C–C bond by 31°; in (XXIII) the CO_2Me groups are assumed to be internally non-planar by the 30° rotations found satisfactory above with, *e.g.*, methyl acetate, and these non-planar CO_2Me groups are themselves rotated by ±30° from that conformation in which the carbonyl bonds are fully *cis* to one another [as given, this description of (XXIII) leads to two models in which the Me • • • Me distances are different; the calculation in Table 14 is for the form with the greater Me • • • Me separation; the other form requires $\mu_{\text{calc.}}$ 3·12 D, which exceeds that observed].



(XX)



(XXI)

TABLE 14.

Semi-axes, component moments, etc., for dimethyl oxalate.

Conformation	Principal semi-axes	Direction cosines with X	Y	Z	Dipole moment components	$10^{12}{}_{m}K$ calc.
(XX) *	1·105	0·9563	0·2924	0	0	$8{\cdot}2_4$
	1·009	−0·2924	0·9563	0		
	0·659	0	0	1		
(XXI) †	1·071	1	0	0	2·49	228·2
	1·043	0	1	0	0	
	0·659	0	0	1	0	
(XXII) †	0·965	1	0	0	2·47	44·0
	1·039	0	1	0	0	
	0·769	0	0	1	0	
(XXIII) †	0·966	1	0	0	2·35	40·8
	1·032	0	1	0	0	
	0·775	0	0	1	0	

* *X* and *Y* in the molecular plane, X parallel to the C=O links. † *Y* axis parallel to the central C–C bond, *X* at 90° to *Y* and lying midway between the planes containing the C=O bonds (cf. cursive text).

Table 14 shows that only conformations (XXII) and (XXIII) are in harmony with both the dipole moment and the molar Kerr constant found by experiment; that the dissolved species is a mixture of (XX) and (XXI), as supposed by Mihazawa and by Saksena,[36] appears unlikely, since the proportions necessary to achieve the observed $\mu_{\text{resultant}}$ would correspond to an $_{m}K$ which is too high or, alternatively, those giving the correct $_{m}K$ would require an apparent moment which is too low. Of forms (XXII) or (XXIII), we prefer the latter because it contains methoxycarbonyl conformations which are consistent with those deduced above for other simple esters.

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[35] Miyazawa and Kurantani, *J. Chem. Soc. Japan*, 1951, **72**, 804.

[36] Miyazawa, *J. Chem. Soc. Japan*, 1954, **75**, 540; Saksena, *Proc. Indian Acad. Sci.*, 1940, *A*, **12**, 416.

Conclusion.—It seems highly probable that the alkoxycarbonyl group occurs generally as a non-planar modification of a planar *s-cis*-precurser, in which the O–C bond of the O–Alkyl group is in a plane which contains the other C–O bond and is itself inclined *ca.* 30° to that in which the O–C=O triangle lies. This angle defines "effective conformations"; it is not meant to deny the possibility of moderate amplitudes of rotatory oscillation of the OR groups, as allowed by electron-diffraction studies. Thus polarity and polarisability indications are that esters as solutes have conformations resembling those adopted by esters as gases.

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