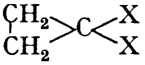
## 304. *The Electric Moments of Cyclic* 1 : 1-*Dicarboxylic Esters in Relation to the Valency-deflexion Hypothesis.*

By E. H. Farmer and N. J. H. Wallis.

In former investigations designed to test quantitatively the validity of the Thorpe–Ingold valency-deflexion hypothesis four physicochemical methods were employed: (1) determination of the heats of formation of 3-, 4-, 5-, etc.-membered rings, (2) determination of the relative ease of fission of *spiro*-compounds, (3) observation of tautomeric equilibria, and (4) determination of the dissociation constants of various 1 : 1-dicarboxylic acids. The failure to obtain decisive evidence for or against the hypothesis renders further observations necessary.

Eucken and Meyer (*Physikal. Z.*, 1929, **30**, 397) have shown mathematically that the group dipole of carbethoxyl can be regarded as a constant if the temperature at which it is measured is constant; rise of temperature, with increased freedom of rotation within the group, should give an increase in the moment. According to Meyer (*Z. physikal. Chem.*, 1930, *B*, **8**, 27), the capacity for free rotation within molecules such as $CH_2Cl{\cdot}CH_2Cl$ and $R{\cdot}CO_2R'$ is diminished by the potential due to the opposed moments of the component groups, and his calculation shows that, when the inner molecular potential exceeds $kT/10$, the rotation should be checked, thus causing the total moment to decrease with fall in temperature. For the carboxyl group (possessing an inner potential energy exceeding $kT$) it is computed that the internal rotation should produce a variation of moment with temperature, the lower limit of the moment being $1{\cdot}1 \times 10^{-18}$ and the upper $3{\cdot}5 \times 10^{-18}$, but the latter value would only be attained at about 20,000°. Smyth (" Dielectric Constant and Molecular Structure," New York, 1931) has drawn attention to the fact that the values of the moment determined at one temperature, and over a short range, for acetic acid and the acetates and formates lie well within these limits (actually near the lower limit) and has suggested that Zahn's measurements for acetic acid vapour between room temperature and 200°, which show an apparent increase in moment from $1{\cdot}4 \times 10^{-18}$ to an average value exceeding $1{\cdot}7 \times 10^{-18}$ (*Physical Rev.*, 1930, **35**, 1047), are possibly to be regarded as evidence in accordance with Meyer's predictions, although Zahn himself attributed the increase to a transition from one state of vibration associated with the OH-group to another. Ethyl acetate (in heptane), however, has been found to show no significant variation of the moment with temperature, even over the range — 70° to 30° (Smyth and Dornte, *J. Amer. Chem. Soc.*, 1931, **53**, 2005).

On the basis of the constancy of the dipole moment of the carbethoxyl group for a given temperature, and taking into consideration Smyth's conclusion that the size of the hydrocarbon radical makes little or no difference to the magnitude of the moment of a monocarboxylic ester (*op. cit.*, p. 94), it becomes possible to approach the valency-deflexion problem from another aspect, since any change in the angle between the carbethoxyl groups in a series of spiran dicarboxylic esters must correspondingly affect the resultant moment due to the carbethoxyl groups (compare Bergmann, Engel, and Wolff, *Z. physikal. Chem.*, 1932, *B*, **17**, 81). Accordingly, the dipole moments of the 1 : 1-dicarboxylic esters of *cyclo*propane, *cyclo*butane, *cyclo*pentane, and *cyclo*hexane (I—IV) have been determined in order to discover whether any systematic variation in the vectorial group-moment of the series could be detected in the sense of the Thorpe–Ingold hypothesis.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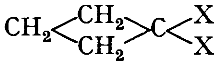
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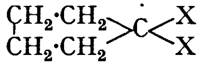
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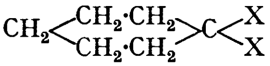
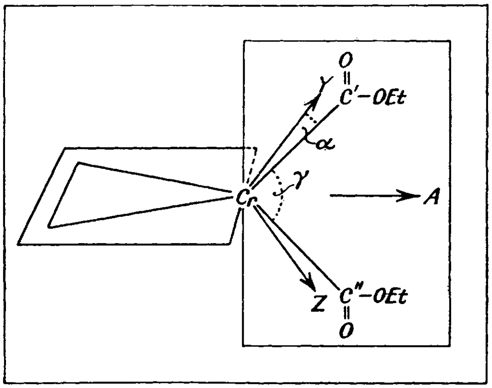

(IV.)

$X = CO_2Et$.

The vectorial group-moment of any of the esters under consideration can be regarded as being made up of two vectors whose actual position within the 1 : 1-dicarbethoxy-group is unknown, but might reasonably be considered to be inclined at an approximately fixed angle (α) to the valency bond between the 1-carbon atom ($C_r$) and the central carbon atom of the carbethoxyl group ($C'$ or $C''$), as shown in Fig. 1.

Fig. 1.



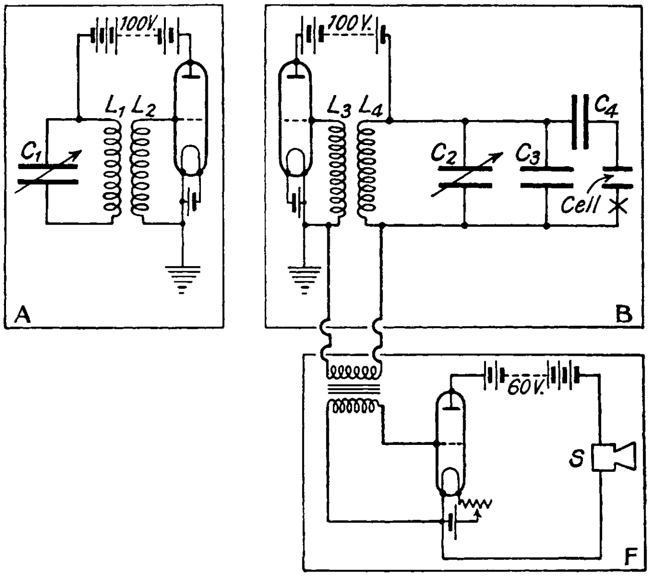
On this assumption, the magnitude of *A*, the summation-moment of the molecule, should increase as $C_rC'$ moves towards $C_rC''$, which should occur, according to the Thorpe–Ingold hypothesis, as the rings become larger. Any increase in the magnitude of the vectorial group-moment of an alicyclic 1 : 1-disubstituted compound with the size of the ring could not be expected to follow quantitatively the values for the external valency angle given by Beesley, Ingold, and Thorpe (J., 1915, **107**, 1080), since the mechanical approach of the two groups would be accompanied by a corresponding electrostatic repulsion, setting up an equilibrium between the ring strain and the repulsion of the groups. The position of equilibrium in each ring system will, however, clearly be different, and this difference should be detected by measurements of the magnitude of the vectorial group-moment $A$.

## EXPERIMENTAL.

Since the changes in dipole moment were expected to be comparatively small, particular attention was paid to the sensitivity of the apparatus employed in the determinations.

*Dielectric Constants.*—In principle, the heterodyne method of Grüssmacher (*Z. Physik*, **1924**, **28**, 342) was employed on account of its greater sensitivity over bridge methods when used with non-conducting dielectrics. Considerable difficulty was experienced at first in obtaining a consistent calibration of the standard Sullivan condenser ($C_2$) to the order of accuracy required; eventually, therefore, a circuit (Fig. 2) was employed which, although giving a small range of capacity change, increased greatly the accuracy of the condenser calibration and the subsequent determination of the dielectric constants.

FIG. 2.



The independent valve oscillators A and B, oscillating at about 4 × $10^5$ cycles/sec., were loosely coupled together. Although the frequency of A could be varied by means of $C_1$, in general it was kept constant. The oscillator B was controlled by a Sullivan standard air condenser, $C_2$, of 0·0012 $\mu$F capacity, fitted with a worm gear slow-motion control and an extension handle 2 m. long; the capacity of this condenser operated through a network of Sullivan fixed mica condensers with a temperature coefficient of $1 \times 10^{-5}$. The existence of a simple relationship between the worm gears of the slow-motion control enabled the condenser to be read to 0·001°, but possible error due to backlash amounted to ± 0·003°, so that 0·01° could be read directly from a circular scale mounted on the driving shaft of the worm gear, the complicated optical arrangements described in the literature thus being dispensed with.

The values of the fixed condensers $C_3$ and $C_4$ were so chosen (0·0015 $\mu$F and 0·002 $\mu$F respectively) as to give a scale " extension " of about four times, and also to give as nearly as possible a linear relationship between the opened and the reduced scales. The scheme was similar to that employed by Ball for a bridge circuit (J., 1930, 577), and enabled an apparent reading of

0·0025° to be made, but considerably restricted the range of capacity changes in the measuring cell (liquids of dielectric constant $>3$ could not be used).

The condensers $C_3$ and $C_4$ were calibrated in terms of $C_2$ by removal from the circuit. Their capacities (each larger than that of $C_2$) were measured by placing them in series with a condenser of about 0·005 μF capacity, which could be determined in terms of $C_2$. $C_4$, which had been specially adjusted by the makers to its value of 0·002 μF, proved to be accurate to 0·1%, $C_2$ being assumed to be 0·0012 μF

The standard condenser $C_2$ was calibrated in steps of about 7° by means of a small variable air condenser, the cell (but not its capacity) and the cell-wiring being in circuit. The reproducibility of the calibration values was of the order of ± 0·004°, but in consideration of the overall accuracy, readings were taken to the nearest 0·01°.

The oscillators A and B were enclosed in a wooden box to prevent great fluctuations in temperature (the principal cause of frequency variation), and the filaments of the valves, and also the water-filled thermostat, were connected to earth. Twisted leads, owing to their constantly changing position relative to the bulk of the apparatus, were avoided, and rigid well-spaced leads, mounted in ebonite to reduce inter-capacity and inductance, were employed; inductance was also combated by keeping the leads as short as possible.

No independent switch was used to remove the cell from circuit, but short flexible copper wires (7/42) were hung from the rigid leads into the mercury cups of the cell, which were filled with pure distilled mercury. The cell was brought in or out of circuit by a defined movement of 5 mm. of one of these wires, so that any capacity change inherent in the switch was negligible. Experimentally it was found possible to move consistently between the same two points on $C_2$ on opening and closing the switch. The capacitance measurements were all accurate to 0·12% and generally to about 0·05%.

The circuits were supplied with high tension current from a large 200 v. block of Exide accumulators of 5000 m. amp. capacity; each low tension circuit was supplied from a separate accumulator.

Resonance was not established between the two oscillators, but a constant difference of 500 cycles was used as a standard condition. This heterodyne note was isolated by tappings on $L_3$ and $L_4$, amplified by the low frequency amplifier F, which energised the loud speaker S. The heterodyne beat note from S was allowed to beat aurally with a note produced from a standard valve-controlled tuning fork oscillating at 500 cycles/sec. This formed a very sensitive arrangement unaffected by stray capacity from the body during manipulation of the apparatus. The rate of creep of frequency was about 2—3 beats per hour when the apparatus had been allowed to oscillate for 3 hours. This drift represents a frequency change of 0·00025%, which was negligible in the time interval necessary to complete the observations.

*The Dielectric Cell.*—The cell, which is described in the paper by Farmer and Warren (p. 1297), was a modification of the Sayce and Briscoe type (J., 1925, **127**, 315). The resistance of the silver films forming the plates was of the order of 1—2ω, and the cell, when filled with benzene, had a resistance between the plates of the order of $5 \times 10^5$ω. The capacity of the cell was about 80 μμF, of which 99·6% was replaceable.

It was found that the level of the water in the thermostat (all the measurements were made at 25° ± 0·01°) affected the capacity of the cell to a small extent (about 0·15% for a large change in level). Although this did not actually matter, since the cell was calibrated immediately before each measurement, it was found convenient in practice to maintain the water level constant.

*Refractive Indices.*—These were measured at 25° for the α-, β-, and γ-hydrogen lines and the $Na_D$ line on a Bellingham and Stanley refractometer for which no calibration (*i.e.*, manufacturers' data) was required, since the refractive index of the prism could be determined on the instrument. The maximum error of measurement lay within ± 0·00004. The refractivities both of the esters and of the benzene solutions of the esters were determined, but the refractivities of the solutions in every case followed closely the simple mixture law and therefore are not here reproduced. It was found possible with the benzene solutions to measure the refractivities in the direction $H_\gamma \longrightarrow H_\alpha$ and $H_\alpha \longrightarrow H_\gamma$ with a change in the angle subtended by $H_\gamma$ of 30″, representing a change of 0·00005 in refractive index. The molecular refractivities for the four lines are given below, also their extrapolation to infinite wave-length by the Cauchy formula. The electron polarisation has, however, been taken as $MR_D$ in order to correct partially for $P_A$, in respect of which the value contributed by the carbethoxyl group is unknown.

*Densities.*—These were measured in a 10 c.c. Pyrex pyknometer of the Hartley type, fitted with external caps and having narrow capillaries. By employing a standard method of treating the pyknometer surface, consistent results agreeing amongst themselves to the fifth significant figure could be obtained.

*Preparation and Purification of Materials.*—The benzene employed as a solvent was purified by successive treatment with concentrated sulphuric acid, potassium permanganate, and sodium carbonate, fractional crystallisation, and fractional distillation over sodium.

The cyclic 1 : 1-dicarboxylic acids were prepared by condensing dibromo-paraffins with sodiomalonic ester (Perkin method), and fractionating and hydrolysing the products. The acids were fractionally crystallised until the recorded m. p.'s (Table I) were attained, and were then esterified with pure alcohol in the presence of a small amount of zinc chloride. The esters, the physical properties of which are given below (Table I), were stored in sealed vessels until required for use.

TABLE I.

*Density and Refractive Index of Cyclic Esters.*

| Acid. | M. p. | Ethyl ester. | | |
|---|---|---|---|---|
| | | B. p. | $d^{25°}_{D}$. | $n^{25°}_{D}$. |
| *cyclo*Propane-1 : 1-dicarboxylic | 136° | 89·5°/9 mm. | 1·05551 | 1·43101 |
| *cyclo*Butane-1 : 1-dicarboxylic | 154 | 108/14 mm. | 1·04264 | 1·43014 |
| *cyclo*Pentane-1 : 1-dicarboxylic | 186 | 97·5/4 mm. | 1·03801 | 1·44203 |
| *cyclo*Hexane-1 : 1-dicarboxylic | 177 | 122·5/13·5 mm. | 1·03515 | 1·44547 |
| Benzene | — | — | 0·87324 | 1·49780 |

The calculation of dielectric polarisation and dipole moment was according to the classical theory of Debye, and the results are shown below.

cyclo*Propane*-1 : 1-*dicarboxylic Ester.*

| $f_2$. | $\epsilon_{25°}$. | $d^{25°}_{4°}$. | $P_{1,2}$. | $P_2$. |
|---|---|---|---|---|
| 0·082600 | 2·8712 | 0·90101 | 37·089 | 150·33 |
| 0·029212 | 2·4887 | 0·88355 | 30·489 | 158·60 |
| 0·014118 | 2·3775 | 0·87821 | 28·519 | 160·15 |
| 0·010320 | 2·3502 | 0·87678 | 28·030 | 161·91 |
| 0·006582 | 2·3227 | 0·87558 | 27·531 | 162·92 |

$P_2$ at infinite dilution = 165·34 cm.³.
$MR_\alpha = 45·37$, $MR_D = 45·65$, $MR_\beta = 46·27$,
$MR_\gamma = 46·69$.
$MR_\infty$ from $MR_D - MR_\beta = 44·37$.
$MR_\infty$ from $MR_\alpha - MR_\gamma = 44·38$.
$P_{A+O} = 119·69$ cm.³; $\mu = 2·40 \times 10^{-18}$ e.s.u.

cyclo*Butane*-1 : 1-*dicarboxylic Ester.*

| $f_2$. | $\epsilon_{25°}$. | $d^{25°}_{4°}$. | $P_{1,2}$. | $P_2$. |
|---|---|---|---|---|
| 0·060218 | 2·6479 | 0·89448 | 33·858 | 146·60 |
| 0·043422 | 2·5475 | 0·88887 | 31·917 | 148·30 |
| 0·014218 | 2·3645 | 0·87856 | 28·398 | 150·70 |
| 0·010844 | 2·3427 | 0·87722 | 27·983 | 151·04 |

$P_2$ at infinite dilution = 151·41 cm.³.
$MR_\alpha = 49·39$, $MR_D = 49·61$, $MR_\beta = 50·31$,
$MR_\gamma = 51·07$.
$MR_\infty$ from $MR_D - MR_\beta = 48·17$.
$MR_\infty$ from $MR_\alpha - MR_\gamma - 48·16$.
$P_{A+O} = 101·80$ cm.³; $\mu = 2·22 \times 10^{-18}$ e.s.u.

cyclo*Pentane*-1 : 1-*dicarboxylic Ester.*

| $f_2$. | $\epsilon_{25°}$. | $d^{25°}_{4°}$. | $P_{1,2}$. | $P_2$. |
|---|---|---|---|---|
| 0·038132 | 2·4883 | 0·88751 | 31·107 | 143·94 |
| 0·013882 | 2·3513 | 0·87852 | 28·265 | 144·12 |
| 0·010367 | 2·3329 | 0·87702 | 27·878 | 146·63 |
| 0·006479 | 2·3105 | 0·87561 | 27·412 | 146·71 |
| 0·003690 | 2·2944 | 0·87446 | 27·082 | 148·04 |

$P_2$ at infinite dilution = 148·95 cm.³.
$MR_\alpha = 54·01$, $MR_D = 54·24$, $MR_\beta = 54·89$,
$MR_\gamma = 55·43$.
$MR_\infty$ from $MR_\alpha - MR_\gamma = 52·96$.
$MR_\infty$ from $MR_D - MR_\beta = 52·92$.
$P_{A+O} = 94·71$ cm.³; $\mu = 2·14 \times 10^{-18}$ e.s.u.

cyclo*Hexane*-1 : 1-*dicarboxylic Ester.*

| $f_2$. | $\epsilon_{25°}$. | $d^{25°}_{4°}$. | $P_{1,2}$. | $P_2$. |
|---|---|---|---|---|
| 0·087993 | 2·8247 | 0·90556 | 38·122 | 157·19 |
| 0·047858 | 2·5798 | 0·89145 | 32·922 | 158·02 |
| 0·030759 | 2·4765 | 0·88553 | 30·798 | 158·93 |
| 0·014329 | 2·3613 | 0·87847 | 28·535 | 159·61 |

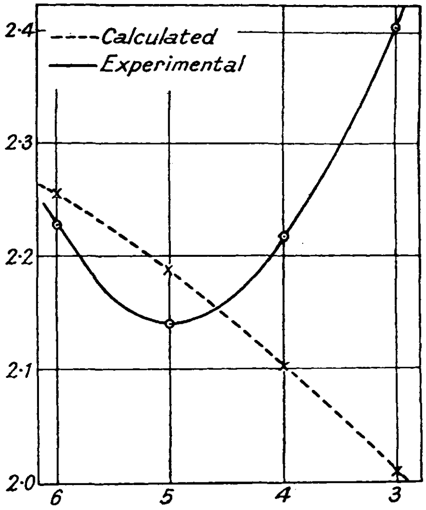
$P_2$ at infinite dilution = 161·44 cm.³.
$MR_\alpha = 58·46$, $MR_D = 58·73$, $MR_\beta = 59·35$,
$MR_\gamma = 59·87$.
$MR_\infty$ from $MR_\alpha - MR_\gamma = 57·42$.
$MR_\infty$ from $MR_D - MR_\beta = 57·44$.
$P_{A+O} = 102·71$ cm.³; $\mu = 2·23 \times 10^{-18}$ e.s.u.

## DISCUSSION.

The observed change in the dipole moment from ring to ring is shown graphically in Fig. 3, and is contrasted with the change in the moment which would be expected to obtain if the external valency angles in the different ring systems were actually those put forward by Beesley, Ingold, and Thorpe (*loc. cit.*). For the purpose of calculating the moments on the latter basis Smyth's value for the moment of the carbethoxyl group, *viz.*, 1·9 × $10^{-18}$ e.s.u. (*op. cit.*, p. 94), is employed.

It will be seen that the magnitude of the group-moments for the 3-, 4-, and 5-membered rings changes in the reverse way to that which would be predicted on the basis of the Thorpe–Ingold hypothesis, and only in passing from the 6- to the 5-membered ring is the direction of change the same. Moreover, the minimum moment occurs in the case of the 5-membered ring, the other rings being grouped in conformity with the Baeyer hypothesis. Thus the results appear to be unfavourable to the Thorpe–Ingold hypothesis. Two contingencies, however, may render this conclusion invalid: (i) the value of the vector group-moment for the carbethoxyl group, here assumed to be constant, may actually change from one ring system to another, and (ii) each carbethoxyl group may tend to rotate about the $C_{\gamma}C'$ and $C_{\gamma}C''$ links with the result that, although the angle $\alpha$ (Fig. 1) will remain constant, the angle between the moments may have a range of values, there being a sort of average probable value determined by the freedom of rotation of the groups and therefore of the moments.

FIG. 3.



The mathematical treatment for a system of this type in which rotation is *completely free* has been given by Fuchs (*Z. physikal. Chem.*, 1931, *B*, **14**, 339). Now it may well be that the freedom of rotation in the spiran esters depends upon the angle between the $C_{\gamma}C'$ and $C_{\gamma}C''$ valencies ($\gamma$ in Fig. 1), increasing when the latter increases, since the carbethoxyl groups are then turned further apart. Increasing freedom of rotation would of itself, other things remaining constant, certainly result in an increase of moment, since the positions of minimum and lower potential energy in such a system are always those of least or lower moment. But any increase in the angle $\gamma$ would of itself cause a decrease in the total moment, provided the freedom of rotation remained fixed. There are then two effects working in opposite directions and it is possible that this may account for the minimum observed in the series of moments recorded above.

A somewhat analogous minimum occurs in the series of dicarboxylic esters examined by Smyth and Walls (*J. Amer. Chem. Soc.*, 1931, **53**, 531). Here the observed moment falls from diethyl malonate to diethyl succinate, rises to diethyl glutarate, and thereafter changes little along the series. The possibility of free rotation about the C—C links of the carbon chain in diethyl succinate and its higher homologues presents an additional complication, but it is conceivable that the minimum possible moment of the molecule decreases on passing from diethyl malonate to diethyl succinate, and that thereafter, in diethyl glutarate and adipate, the freedom of rotation increases and so does the moment. The moment of diethyl malonate, 2·54, is greater than any of those reported in this paper and in this substance the carbethoxyl groups would be expected to be farthest apart.

In order to gain further information respecting the above contingencies, the dipole moments of (*a*) a series of cyclic monocarboxylic esters and (*b*) a series of spiran diacetic esters in which the mutual influences of the polar groups should be less powerful than in the examples considered in the present paper, are now under investigation.

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