300. *Evidence of Wave-mechanical Resonance in the Carboxylic Ester and the Lactone Group, from Electric Dipole Moments.*
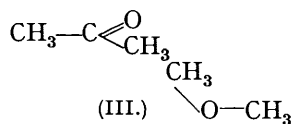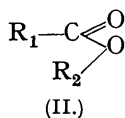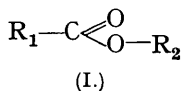
By RALPH J. B. MARSDEN and L. E. SUTTON.

FEW groups of compounds have been more assiduously and systematically investigated than the carboxylic esters. The main results of the electric dipole moment measurements made upon them are summarised below : Table I gives the moments for most of the mono-esters, $R_1 \cdot CO_2R_2$, and Table II shows the effect of temperature upon the moments of a few of them. (All values are in Debye units, D, *i.e.*, e.s.u. $\times 10^{-18}$, here and throughout.) In Table I the italicised figures are the results of vapour-phase measurements; the others relate to solutions in benzene (this being the most commonly used solvent) uncorrected for atom polarisation in order that they may be comparable. The values are weighted means of those given in the " Table of Dipole Moments " (Sidgwick *et al.*, *Trans. Faraday Soc.*, 1934, **30**, Appendix).

TABLE I.

R_2/R_1.	H.		CH_3.		C_2H_5.	C_3H_7.	C_4H_9.	$C_{13}H_{27}$.	C_6H_5.	$p\text{-}C_6H_4Me$.	$CHPh{:}CH_2$.
CH_3	—	—	1·78	*1·67*	1·74	1·77	1·68	1·74	1·91	2·12	—
C_2H_5	1·94	*1·92*	1·85	*1·76*	1·80	1·81	—	—	1·92	—	2·14
$n\text{-}C_3H_7$	1·93	—	1·86	—	1·83	—	—	—	—	—	—
iso- ,, ...	—	—	1·89	—	—	—	—	—	—	—	—
$n\text{-}C_4H_9$	—	—	1·90	—	1·85	—	—	—	—	—	—
iso- ,, ...	1·93	—	1·91	—	—	—	—	—	—	—	—
tert.- ,, ...	—	—	1·96	—	—	—	—	—	—	—	—
C_5H_{11}	—	*1·90*	1·91	*1·70*	—	—	—	—	—	—	—
iso- ,, ...	—	—	1·89	—	—	—	—	2·2	—	—	—
cyclo-C_6H_{11} ...	—	—	1·90	—	—	—	—	—	—	—	—
sec.-C_8H_{17} ...	—	—	1·93	—	—	—	—	—	—	—	—
l-Menthyl ...	2·15	—	1·93	—	1·90	1·81	—	—	—	—	—
l-Bornyl	2·13	—	1·98	—	1·95	1·92	—	—	—	—	—
CH_2Ph	—	—	1·89	—	—	—	—	—	—	—	—
C_6H_5	—	—	1·59	—	1·62	—	—	—	1·91	—	—
$p\text{-}C_6H_4Me$ ...	—	—	1·63	—	—	—	—	—	—	—	—

Eucken and Meyer (*Physikal. Z.*, 1929, **30**, 397) remarked that the magnitudes of the ester moments show that the average configuration of the group is nearer (I) than (II).

$$R_1\!-\!C{\overset{O}{\underset{O-R_2}{\big<}}} \qquad R_1\!-\!C{\overset{O}{\underset{\underset{R_2}{\diagup}}{\big<}}}O \qquad CH_3\!-\!C{\overset{O}{\underset{\underset{CH_3}{CH_3}}{\big<}}} \quad \diagdown O\!-\!CH_3$$

(I.)   (II.)   (III.)

Using the scanty data then available, they calculated the moments of these two configurations to be 1·1 and 3·4 respectively. The calculation may be performed very simply, without the preliminary analysis into bond moments, which these authors used, for, provided that no interaction occurs between the ether and the carbonyl groups, the moment of, say, methyl acetate is the resultant of those of dimethyl ether and of acetone at an angle ϕ determined by the configuration (see III). As may readily be seen, ϕ is 180° for configuration (I) and $180° - 2(180° - 125\cdot25°) = 70\cdot5°$ for configuration (II), the van't Hoff model for

the carbon and oxygen atoms being assumed (cf. Sutton and Brockway, *J. Amer. Chem. Soc.*, 1935, **57**, 473). Since ϕ is greater in the former than in the latter configuration, these may be called the *trans-* and the *cis-*configuration respectively. Now, the moments of dimethyl ether and acetone being 1·32 and 2·85 respectively in the vapour phase (see " Table of Dipole Moments," *loc. cit.*), the moments of the two configurations are 1·53 and 3·53. The actual value is 1·67, and therefore the actual configuration almost certainly approximates to the *trans*-one.

Strictly speaking, however, this proof of configuration is imperfect, for it is not inconceivable, although unlikely, that some interaction might considerably reduce the moment of the *cis*-configuration. The proof would be complete if it could be shown that a compound in which the ester group is known from other considerations to be fixed in the *cis*-position actually has a moment of 3—4. γ-Lactones are such compounds, for it is known that they have a five-membered ring structure which provides the required constraint. The moment of γ-butyrolactone was therefore measured : it is 4·12, *i.e.*, even larger than the upper calculated value, and thus it confirms Eucken and Meyer's conclusion. The approximate configuration having thus been finally settled, the question of the exact configuration may now be discussed.

Zahn (*Physikal. Z.*, 1932, **33**, 730) has shown convincingly that the moments of several carboxylic esters are independent of temperature over ranges of 140—190° and at temperatures up to 243° (see Table II), and therefore that the molecules do not rotate appreciably from out of a fixed configuration, which we now know definitely to be the *trans*-configuration. Our next task is to explain this fact.

TABLE II.

Substance.	Temp. range, ° Abs.	Mean moment.	R.m.s. deviation.
Ethyl formate	292·4—434·5°	1·92	0·012
Amyl formate	375·8—516·4	1·90	0·0009
Methyl acetate *	327·3—516·4	1·67	0·013
Ethyl acetate	302·2—466·6	1·76	0·000
Amyl acetate *	376·0—516·8	1·70	0·015

* These substances showed slightly lowered moments at the *higher* temperatures, which was ascribed by Zahn to association at lower temperatures.

Meyer (*Z. physikal. Chem.*, 1930, **B, 8**, 27) calculated that the electrostatic forces between the carbonyl and the hydroxyl bond moments would suffice to lock the carboxylic acid group rigidly at all ordinary temperatures, and since the moment of the methoxyl group is not greatly different from that of hydroxyl (about 1·61 and 1·51 respectively, angles of 110° and 105° being assumed in dimethyl ether and water respectively), the same should be true of the ester group. Sturtevant (*J. Amer. Chem. Soc.*, 1933, **55**, 4478), treating the problem more exactly, and also using different assumptions in locating the bond dipole, concluded that locking would not be complete. Zahn (*Trans. Faraday Soc.*, 1934, **30**, 804) and Sutton (*ibid.*, p. 789; in this paper the terms *cis-* and *trans-* were used in the opposite, less logical sense) therefore suggested that the rigidity is due to wave-mechanical resonance of the classical structure (IV) with an excited one (V), for then the C—O bond in the actual

" mesomeric " molecule would have in part the character of a double bond, and rotation about it as an axis would consequently be restricted. This conception is discussed more quantitatively on p. 1387; at this stage it may be left as a qualitative idea. Such an effect would only make the molecule tend to assume either the *cis-* or the *trans*-position, not favouring either, but there is no doubt that, even if the electrostatic forces are not the major cause of the fixation, they are nevertheless considerable, and would make the *trans*-configuration considerably the more stable of the two which the resonance effect would allow. The possible energy relations are shown diagrammatically in Fig. 1.* The actual

* To illustrate this point the curves $V = a \cos \xi + b \sin (2\xi - 90°) + 5$, with a and b, 5, 0 ; 4, 1 ; 4, 1 ; 3, 2 ; 2, 3 ; 1, 4 ; and 0, 5 have arbitrarily been used.

curve would be a combination of the electrostatic curve, 1, and the resonance one, 6 : various possibilities, corresponding to different degrees of relative importance, are depicted. The configurations are characterised by ξ, the angle between the projections of the C=O and the O—C bond moments on a plane perpendicular to the C—O axis of rotation.

It is obviously desirable to obtain further evidence to prove or disprove this hypothesis, and in view of the uncertainties in such calculations as those made by Meyer and Sturtevant, it seemed advisable to employ a fresh method of attack.

Inspection of a space model of the classical formula of an ε-lactone shows that the lactonic ester group is no longer constrained in the *cis*-configuration by the ring but is free to rotate some way round towards the *trans*-configuration. The seven-membered ring may exist in either of two forms related respectively to the cradle and chair (or *C* and *Z*) forms of a non-planar six-membered ring : both, however, are flexible. By rotation alone about single bonds, the *C*-form permits the lactone group to rotate through approximately 80—85° either way from the *cis*- towards the *trans*-configuration : in the *Z*-form it may rotate through approximately 105° either way (see Fig. 2). Rotation beyond these respective limits would bend valencies and would therefore bring in another kind of potential energy.

Fig. 1.

Thus, in order to obtain the complete potential energy–configuration curve for an ε-lactone, a curve to represent this bending energy, having zero values within the region $\xi < 90°$ or $> 270°$ but considerable values within the region 90—270°, would have to be superimposed upon the curves in Fig. 1, with the possible results shown in Fig. 3.* Curve
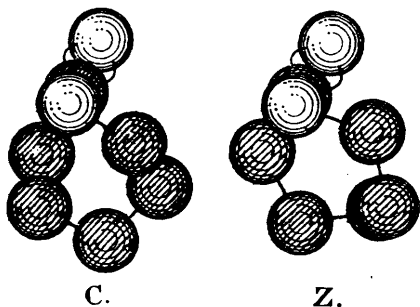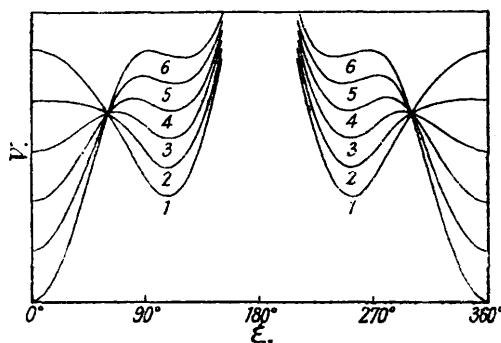
Fig. 2.

C. Z.

Fig. 3.

I shows minima at the equivalent configurations $\xi = 90$—135° and $\xi = 225$—270°. The calculated value of the moment for the 90° configuration is 2·7, and therefore, if Curve I were qualitatively correct, *i.e.*, if there were only electrostatic and valency bending energies to be considered, the observed moment should be 2·7 or less. If, however, torsional energies have to be included as a result of the resonance or mesomerism suggested, then the actual relation would be that represented by one of the curves 2, 3, 4, 5, and 6, according to the relative importance of this third energy. As this increases, the minima at $\xi = 90$—135° and 225—270° disappear, while one at the *cis*-configuration ($\xi = 0°$) appears, and therefore the observed moment would approach the value of 4·1 found for the γ-lactone.

It must be pointed out that there are other possible sources of configurational energy in such a molecule, and for the sake of completeness these should be taken into account.

* These are obtained by adding half of the parabola $V = a\ (\xi - 90°)^2$ and half of $V = a(270° - \xi)^2$, $(a = 1/400)$, to the curves in Fig. 1.

They arise from the repulsions between atoms less than about 3·5 A. apart, and from the " dispersion force " attractions between atoms more than this distance apart (Eyring, *J. Amer. Chem. Soc.*, 1932, **54**, 3191 ; Teller and Weigert, *Nach. Ges. Wiss. Göttingen*, 1933, 218 ; Eucken and Weigert, *Z. physikal. Chem.*, 1933, *B*, **23**, 265 ; London, *Z. Physik*, 1930, **63**, 243 ; *Z. physikal. Chem.*, 1930, *B*, **11**, 222). The former forces occur between atoms which are bonded to adjacent ring atoms, and which may therefore be themselves either members of the ring or atoms attached thereto. Consequently, rotation about the bonds in the ring would be partly restricted, as it is about the central bond in ethane. The depth of the potential-energy trough in ethane is about 380 cals./g.-mol. and the values in the more complex cases which we are considering would probably be of the same order ; the rotation about the carbon–oxygen links would, however, be less restricted because oxygen has a smaller valency. It would therefore appear that the maximum energy restricting free flexing might be as much as 2,000 cals./g.-mol. Examination of a space model shows, however, that this would not actually be so. In either the *C*- or the *Z*-form the ring has the same shape (provided that no differentiation be made between oxygen and carbon atoms) in the *cis*-configurations and in those nearest to the *trans*-configurations, as shown in Fig. 4.

FIG. 4.
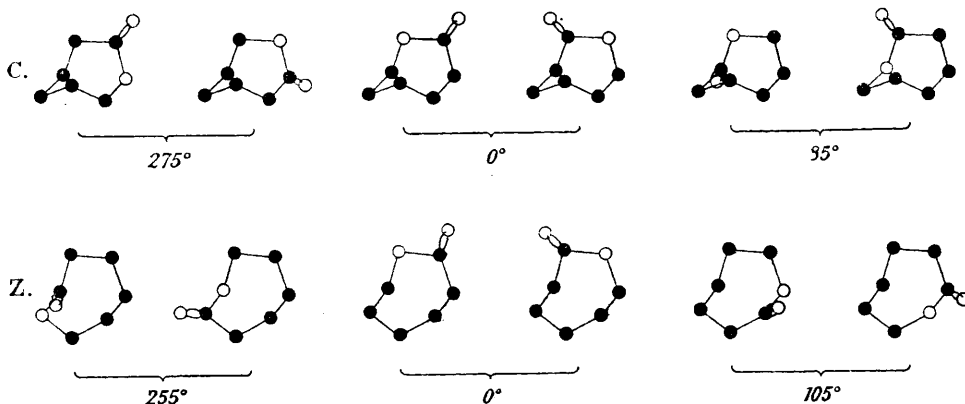
This happens also at various intermediate configurations. Now, were it a *cyclo*heptane ring, these would all be configurations of equal repulsion energy ; it actually differs from this only by the nature of two of the seven atoms, and so, although there are variations in repulsion energy, they are small. They may be very roughly assessed by estimating the repulsion energies about each bond, counting them as maximum, minimum, or intermediate, and summing them all. Then, taking the maximum repulsion energy about one bond as a unit, it is found that the differences in energy between the extremes allowed by valency rigidity are not more than about one unit, *i.e.*, 400 cals./g.-mol.

It is even less easy to estimate how the dispersion force energy would vary with configuration, but, unless groups attached to the ring may complicate the question, differences could only arise from variations of the distance between the carbonyl oxygen and four of the ring atoms. For such light atoms no energy differences greater than about 300 cals./g.-mol. would be anticipated.

The ε-lactone most readily available appeared to be βζ-dimethyl-ε-octolactone (VI) (Baeyer and Seuffert, *Ber.*, 1899, **32**, 3622 ; Baeyer and Villiger, *ibid.*, p. 3625), and accord-

$$CH_2 \begin{array}{c} CHMe—CH_2—CO \\ \diagup \qquad \qquad \diagdown \\ \diagdown \qquad \qquad \diagup \\ CH_2·CH(CHMe_2)·O \end{array}$$

(VI.)

ingly this substance was made and examined. The electric dipole moment is 4·33, *i.e.*, not less, but 0·21 more than the moment of γ-butyrolactone, and it is therefore clear that the molecule is rigidly held in the *cis*-configuration ; from the foregoing arguments it follows that the only torsional energy which would be of the right kind or magnitude to do this is that arising from resonance or mesomerism. We may therefore conclude that the fixation in both esters and lactones is caused mainly by this phenomenon.
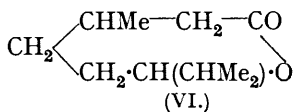
Resonance *cum* mesomerism may cause the magnitude and direction of the moment of a molecule to be abnormal (Sutton, *loc. cit.*), and so it would be expected that this would occur in the esters and lactones. The calculated moments for the *trans-* and the *cis-*configuration are 1·53 and 3·53 respectively (see p. 1384), whereas the actual values are 1·7—1·9 and 4·2 respectively; the numerical abnormalities are therefore 0·17—0·37 and 0·69 for the two groups. Thus there is indeed a perceptible, though small, abnormality for the ester group, and a considerable one for the lactone group. The actual mesomeric moments are probably larger than these values for two reasons. (i) Because the effect of mutual induction between the carbonyl and the ether group, which has not been taken into account, would be to reduce the calculated moments and so to increase the above differences; no quantitative allowance can be made for this, because the groups are so near, but it may be seen that it would be greater for the ester than the lactone. (ii) Because the direction of the mesomeric moment, involving as it does the transference of part of an electronic charge from the ethereal to the carbonyl oxygen, is not collinear with the total moment of either group. This would affect the mesomeric moment calculated for the lactone more than that for the esters.* On the basis of the bond lengths and angle specified in the footnote, the oxygen atoms would be 2·33 A. apart, and the moment due to a complete transference of an electron from one to the other would be $2·3 \times 4·77 \doteqdot 11·04$.† The moment, μ, of the actual molecule would be the resultant of three (one for each spatial co-ordinate), each given by an expression

$$\mu_x = \alpha_1{}^2\mu_{1x} + \alpha_2{}^2\mu_{2x} + 2\alpha_1\alpha_2\int\psi_1\mu\psi_2.d\tau$$

(α_1, ψ_1, μ_1 referring to the first, or ordinary structure, and α_2, ψ_2, μ_2 to the second, the excited, highly polar structure), in which the third, or cross term is probably less important than the sum of the other two (Sutton, *Trans. Faraday Soc.*, 1934, **30**, 789) and may, to a first approximation, be neglected. Hence, from $\mu - \mu_1$ and $\mu_2 - \mu_1$ it is possible to calculate a rough value of $\alpha_2{}^2/(\alpha_1{}^2 + \alpha_2{}^2) = \alpha_2{}^2$, *i.e.*, of the fractional importance of the excited structure in the molecule. In the present case this fraction is $0·94/11·04 \doteqdot 1/12$. This means that the structure (V) is only about one-eleventh as important as the classical structure in the make-up of the molecule, and hence it is of the same order of importance as are similar excited structures in monosubstituted benzene derivatives (Sutton, *loc. cit.*). It may be noted that the resonance energy in the ester group,‡ which is 17—28 kg.-cals./g.- mol., is also of the same order as those found in benzene derivatives, which vary from 5 to 12 kg.-cals./g.-mol. It is reasonable to assume that, if the excited structure is one-twelfth of the actual molecule, the energy necessary to rotate the two halves of the group from the *trans-* or the *cis-*configuration to half-way between them (apart from that necessary to overcome the electrostatic forces) is at least one-twelfth of that necessary to twist a pure double bond. Unfortunately, there are no data which show exactly what the latter is, but there are two ways of getting some idea of it. (i) Warburg's (*Ber. Berl. Akad.*, 1919, 960) on the interconversion of fumaric and maleic acids by ultra-violet light showed that the quantum necessary was not more than 95 kg.-cals./g.-mol. (corresponding to $\lambda = 300$ mμ). (ii) By assuming that a double bond twisted 90° from a resting position is in effect only a single bond, we may conclude that the energy necessary to do this would be the difference of their heats of formation, which from Pauling and Sherman's values (*J. Chem. Physics*, 1933, **1**, 606) for C=C and C—C is 67 kg.-cals./g.-mol., or for C=O and C—O is 91 kg.-cals./g.-mol. Since these two different methods give results of the same order of magnitude, it is reasonably certain that they give the order of the correct result. The twisting energy in the

* Taking the C=O and the C—O distance as 2·60 A. and 1·30 A. (to allow for some shortening, see Pauling, *Proc. Nat. Acad. Sci.*, 1932, **18**, 293; 1934, **20**, 336) and the angle O=C—O as 125°, and using the moments already quoted, the corrected mesomeric moment for the lactone group is found to be 0·94.

† Since the actual moments of co-ordinate links, 2·5—4, are invariably much less than the values of 7—10 calculated in such a manner, the values taken for μ_2 may be too great, and the calculated value of $\alpha_2{}^2$ too small.

‡ The resonance energy in lactones cannot be calculated with any accuracy from existing data, for no simple, uncomplicated lactones have had their heats of combustion determined. What data there are, however, indicate that it is at least as great as that in the esters.

actual molecule would therefore be about 5·5—7·5 kg.-cals./g.-mol., a result which is of the right order to explain the observed fixation. It must be emphasised that this figure was obtained through a considerable approximation and an *ad hoc* assumption, but it is probably of sufficient significance to show that the various data are consistent. Since it is less than the resonance energy (17—28 kg.-cals./g.-mol.), the perturbation which could be caused by even a considerable twist would not suffice to reduce the coefficient of the excited structure to zero, although it would cause some reduction and the twisting strain energy would thereby be reduced (cf. Sutton and Pauling, *Trans. Faraday Soc.*, 1935, **31**, 939).

In view of the foregoing conclusions, Wolf and Gross's suggestion (*Z. physikal. Chem.*, 1931, *B*, **14**, 305) that the variations in moment of the aliphatic esters are due to variations of orientation of the group must be regarded as improbable, especially as the increase with temperature of the moments of *sec.*- and *tert.*-alcohol esters, which was anticipated from this idea, has not been demonstrated. Instead, it may be suggested that the variations (which are shown both by vapour-phase and by solution moments) are due to simple electrostatic induction, to change in the relative importance of the excited form, or to both of these causes. The variations in moment of the aromatic esters would, similarly, be due to these causes and also to the existence of excited structures involving the benzene ring, or rings. As Robinson (*Rapp. Inst. Intern. Chim. Solvay*, 1931, 423) and Ingold (*Chem. Reviews*, 1934, **15**, 225) have pointed out, the ester group should have a dual character ; in benzoic esters ($R_1 = Ph$) it should be *m*-directing, but in phenolic esters ($R_2 = Ph$) it should be *op*-directing : either type of behaviour should be less marked than for the carbonyl or the ether group alone, owing to the interaction within the group itself. Now, the facts are that the moments of methyl esters of aliphatic acids vary from 1·68 to 1·78 in benzene solution, whereas that of methyl benzoate is 1·91. This, and the moment of methyl *p*-toluate, 2·12, show that the moment of the carbomethoxy-group is negative relative to the benzene ring (Sutton, *loc. cit.*), and hence the algebraic difference $\mu_{arom.} - \mu_{aliph.}$ is $- 0.13$. Owing to the asymmetric nature of the group, this is not the vector difference ; a rough calculation gives this as $- 0.2$. The negative interaction moment is qualitatively what would be predicted for such a *m*-orienting group, and it is, moreover, satisfactory that it should be numerically less than that of $- 1.05$ estimated for benzaldehyde. The moment of ethyl cinnamate, 2·14, indicates an interaction moment of *ca.* $- 0.4$ in this compound. The moment of phenyl acetate, however, is anomalous, inasmuch as it is only 1·59, *i.e.*, less than that of methyl acetate, whereas the anticipated positive interaction moment with the benzene ring on the oxygen atom would be roughly parallel to the negative one in methyl benzoate, and should similarly increase the total moment. The decrease is not due to the greater polarisability of the alcohol group, because the moments of *sec.*- and *tert.*-esters are greater, not smaller, than those of methyl esters. The moment of phenyl benzoate, 1·91, differs more from that of phenyl acetate, 1·59, than does that of methyl benzoate, 1·91, from those of the methyl esters of aliphatic acids, 1·68 — 1·78 : this indicates that the carbonyl group acts more independently of the ether group in this compound. With one exception, therefore, these results are in accord with the predictions of theories based on chemical evidence.

The heats of formation of some of these esters afford further evidence of interaction between the group and the benzene ring. For instance, in methyl benzoate, methyl cinnamate, and phenyl benzoate there is an excess of about 7—8·5 kg.-cals./g.-mol. over the resonance energy of the aliphatic ester group plus that in the benzene ring, or rings (1·62 v.-e. = 37·35 kg.-cals./g.-mol.). Phenyl acetate has not been measured, but vinyl acetate shows a similar excess of 7·4 kg.-cals./g.-mol. and eugenol acetate, compared with *m*-tolyl methyl ether, an extremely large one of 33·8 kg.-cals./g.-mol.

In conclusion, a *résumé* of what can be said about the configuration of the nitrous esters may be given. Values of the moments for the *trans-* and *cis*-configurations may be calculated roughly from the moments of 2-nitroso-2 : 5-dimethylhexane, 2·51, and of dimethyl ether, 1·32, it being assumed that the moment of the O—N bond is the sum of those of the O—R and R—N bonds, and that the moment of the nitroso-compound acts at an angle of 148° relative to the R—N bond (Hammick, New, and Sutton, *J.*, 1931, 742). They are 1·39 and 2·77 respectively. The observed moments of ethyl and propyl nitrites in benzene

solution are 2·20 and 2·28 respectively, *i.e.*, they are not close to either value but somewhat nearer that for the *cis*-configuration. If, in order to improve the calculation, the moment of the nitroso-compound be corrected for solvent effect, by applying the same factor as that found for nitromethane, the calculated moments for the *trans*- and the *cis*-state become 1·70 and 3·06 respectively. The moment found for ethyl nitrite in the vapour phase, 2·38 (Czerlinsky, *Z. Physik*, 1934, **88**, 515), falls midway between these values. At present, therefore, the dipole moments do not establish the configuration of the nitrous esters. It is probable that the molecule actually is fixed in the *trans*-position, but that the excited structure is so important that it increases the moment of the molecule to the large, observed value. The interaction moment in *p*-nitrosophenol, which should be comparable, is about 1·12. This hypothesis might be tested by investigating the temperature sensitivity of the moment. Stuart and Volkmann (*Ann. Physik*, 1933, **18**, 121) attempted to determine the configuration from the Kerr effect, but since they assumed that the single and double bonds of the nitrogen atom are collinear, which is now known definitely not to be the case (Hammick, New, and Sutton, *loc. cit.*), their conclusions need revision.

<center>EXPERIMENTAL.</center>

Preparation and Purification of Materials.—Benzene was purified as described by us (this vol., p. 604).

γ-Butyrolactone. This was prepared by the method of Boorman and Linstead (J., 1933, 578) from trimethylene chlorohydrin ("Organic Syntheses," Vol. 8, 112). The distilled product (b. p. 88·5—90·5°/20 mm.) was redistilled shortly before being used for dipole-moment measurements; b. p. 84—86°/12 mm. (Boorman and Linstead, *loc. cit.*, give 83·5°/12 mm.). The substance was recovered from each benzene solution after measurement, and since any water would distil off with the benzene, it was thus kept dry.

βζ-Dimethyl-ε-octolactone (VI). 38 C.c. of *l*-menthone (b. p. 210—212°), obtained by the oxidation of *l*-menthol, m. p. 46°, $[\alpha]_D = -50·55°$, by potassium dichromate and sulphuric acid (Beckmann, *Annalen*, 1899, **250**, 325), were dissolved in ligroin (b. p. 60—80°) and treated with a cold, filtered solution of 200 g. of potassium persulphate, 94 c.c. of water, and 278 c.c. of concentrated sulphuric acid. The mixture was stirred vigorously and kept cooled below 15° (cf. Ruzicka and Stoll, *Helv. Chim. Acta*, 1928, **11**, 1159; Baeyer and Villiger, *loc. cit.*). The mixture was poured on ice, extracted with ether, and the ether–ligroin layer washed thrice with sodium carbonate solution and then with water, dried over anhydrous magnesium sulphate, the solvent evaporated off, and the residue distilled under reduced pressure, giving fractions : (i) below 140°; (ii) 140—149°; (iii) 149—157°/30 mm. Fraction (iii) solidified immediately on cooling in ice and salt, and stirring; fraction (ii) solidified on cooling and "seeding" but largely re-melted on warming. The preparation was repeated thrice, and the products which solidified in ice-water were combined and filtered free from oil; yield 8·5 g. Recrystallisation of this product from slightly aqueous methyl alcohol failed to give a product melting above 36—36·5° (Baeyer and Villiger, *loc. cit.*, give 46—48°; Baeyer and Seuffert report two modifications, m. p.'s 8—10° and 47°), which was very hygroscopic. The material, together with that recovered from the mother-liquors, was twice redistilled in a vacuum, and the main fraction obtained crystallised at once in the receiver as long white hygroscopic needles. Just before use, this was dissolved in a little pure benzene, the benzene and traces of water distilled off, and the residue again fractionated in a vacuum, the fraction, b. p. 142—145°/18—20 mm., being used; yield 4·5 g. This also was recovered from each solution after measurement.

Determination of Electric Dipole Moments.—The measurements were made in benzene solution at 25·0°, as before described (*e.g.*, Marsden and Sutton, *loc. cit.*), and the same values were taken for the constants used. The densities denoted by asterisks are corrected values from the mean density–f_2 curve.

f_2.	$d_4^{25°}$.	ϵ.	n^2.	P_2.	$_EP_2$.	f_2.	$d_4^{25°}$.	ϵ.	n^2.	P_2.	$_EP_2$.
		γ-Butyrolactone.						*βζ-Dimethyl-ε-octolactone.*			
0·00000	0·8734	2·2727	2·2571	—	—	0·00000	0·8738	2·2727	2·2571	—	—
0·01312	0·8766	2·5872	2·2562	349·1	20·7	0·01355	0·8765	2·6325	2·2548	416·2	48·9
0·01560₅	0·8772	2·6475	2·2563	345·3	21·0	0·02139	0·8780	2·8468	2·2524	406·2	48·1
0·02750	0·8802*	2·9297	2·2544	324·4	20·2	0·02577	0·8788₅	2·9596	2·2521	396·9	48·4
0·03065	0·8810*	3·0011	2·2538	318·4	20·0						

<center>

$^\infty P_2 = 373 \pm 4$ c.c.; $^\infty_E P_2 = 21·1$ c.c.;

$\mu = 4·12$.

$^\infty P_2 = 437 \pm 5$ c.c.; $^\infty_E P_2 = 48·5$ c.c.;

$\mu = 4·33$.

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SUMMARY.

(1) The calculated moments (in Debye units) for the two extreme possible configurations of the carboxylic ester group are 1·53 for the *trans-* (alkyl groups as far apart as possible) and 3·53 for the *cis-* (alkyl groups as near as possible). From these values, and the facts that the moment of γ-butyrolactone is 4·12, and that the lactone has the *cis*-configuration, it is now proven that the esters must have the *trans*-configuration.

(2) If the very definite *trans*-fixation observed in esters were due to electrostatic forces alone, the moment of an ϵ-lactone should be approximately 2·7; if, however, it were due mainly to stiffening produced by resonance with another structure, the moment should be at least equal to that of a γ-lactone. That of $\beta\zeta$-dimethyl-ϵ-octolactone is slightly larger, 4·33, and thus supports the latter explanation.

(3) The evidence which the moments of the phenolic and benzoic esters afford of resonance interaction with the benzene ring is discussed, and shown to support the predictions of the Robinson–Ingold theories.

(4) The configuration of the nitrous esters is discussed. The available experimental evidence is not decisive.