THE DIPOLE MOMENT AND STRUCTURE OF PYRONES.

2·6 Dimethyl-γ-Pyrone, Xanthone and Coumarin.

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THE pyrones are an important class of organic compounds containing a six membered heterocyclic ring of five carbon atoms and one oxygen atom, one of the carbon atoms having formed a ketonic group. There are two isomeric forms possible, the α-pyrones and the γ-pyrones, whose constitutional formula in which the atoms exhibit normal co-valencies are I and II respectively.
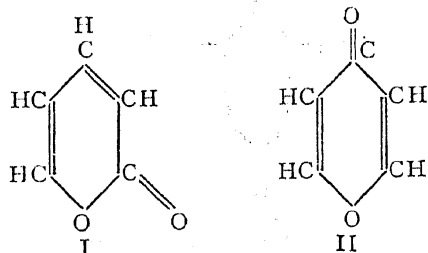
The commonest representative of an α-pyrone is benzo-α-pyrone or coumarin, the aromatic principle of wood-ruff and other plants : the γ-pyrones on the other hand are found even more extensively in nature as yellow colouring matters and also in opium. A special feature of the properties of all these pyrones, is that the carbonyl groups present in them do not exhibit their usual chemical reactivity such as the formation of oximes and phenyl hydrazones. An even more marked feature is a feeble basicity which they exhibit and build as a consequence a number of characteristic salts. These properties of the pyrone-ring have been the subject of considerable interest for a long time and a variety of investigations on the chemical and physical properties of these compounds have resulted, until recently, in the formulation of several different structures, on none of which however there has been a general agreement.[1] All these formula can, in general, be grouped into (i) those in which the ring oxygen atom alone exhibits quadrivalency, (ii) those in which the carbonyl oxygen alone exhibits quadrivalency, (iii) those in which both oxygen atoms exhibit quadrivalency and a whole series of other formula (iv), (v), (vi) according to which the pyrones form co-ordination compounds.

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[1] Beilstein, *Handbuch der Organische Chemie*, 4th Edition, Band XVII, 1933, p. 268.

(i)   (ii)   (iii)   (iv)   (v)   (vi)
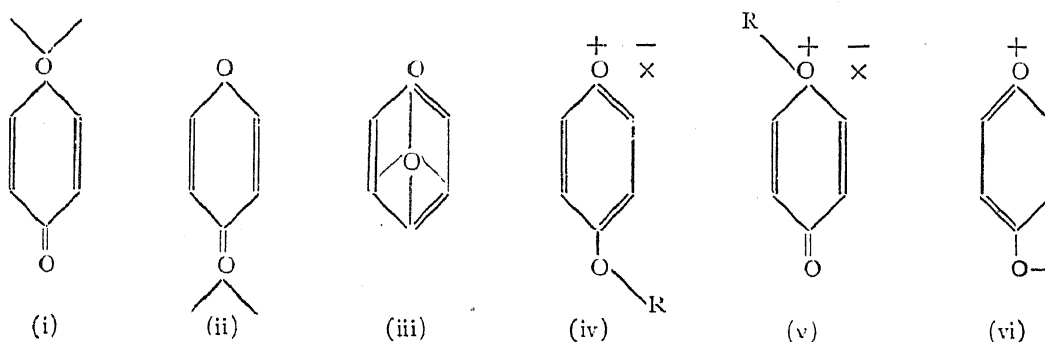
Among some of the elegant experiments in favour or against any of these formulæ may be mentioned the observation of Gibson and Simonsen[2] about the non-resolvability of 2 phenyl 6 methyl-4-pyrone-d α-camphor sulphonate
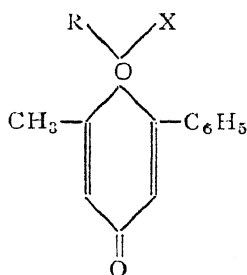
thus disproving formula (i), and the experiment of Bayer[3] by which the methiodide of dimethyl-γ-pyrone could be readily transformed to methoxy lutidine and so must be represented by formula (iv).
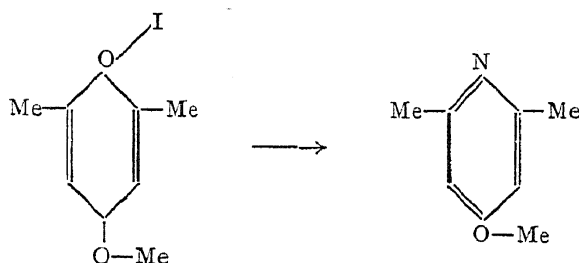
The evidences provided in this connection by the study of the absorption spectra of pyrones and their salts have been rather indefinite.[4] An elimination of a number of these hypothesis, and a definite orientation of ideas has been possible since the advent of the electromeric theories of structure developed by Robinson,[5] and the quantum-mechanical resonance theory

[2] C. S. Gibson and J. L. Simonsen, *Jour. Chem. Soc.*, 1928, 2307.

[3] A. Bayer, *Ber.*, 1910, 43, 2337.

[4] A. A. Boon, F. J. Wilson and I. M. Heilbron, *Jour. Chem. Soc.*, 1914, 105, 2177.
A. Hantsch, *Ber.*, 1919, 52, 1535.
R. C. Gibbs, J. R. Johnson and E. C. Hughes, *Jour. Amer. Chem. Soc.*, 1930, 52, 4895.

[5] R. Robinson, *Outline of an Electrochemical Theory of Course of Organic Reactions*. Institute of Chemistry Lecture, 1932.

of molecular structure developed by Pauling,[6] and it is now definitely considered that the true state of the pyrone molecule is an intermediate one between the ketonic and the betain-like ionised form (vi).[7] A considerable support to this view has been provided by the dipole moment measurements of Partington,[8] who found for dimethyl γ-pyrone a moment value much higher than that calculated for the usual ketonic formula. The object of the present investigation is to verify and more fully interpret these dipole moment measurements for a series of similar compounds.

Experimental.

The moments were measured by the method of dilute solutions, using benzene as solvent, and over a range of 10° to 40° C. The test condenser used in the dielectric constant measurements, the methods of filling and handling the same, were exactly as described in a previous paper,[9] excepting that the capacities were measured in a heterodyne apparatus, instead of in the bridge circuit previously employed. In the present apparatus, a screened-grid valve oscillator was employed, and it was stabilised as described by Schweimer and Pungs[10] by adjusting the ratio between the screened-grid and anode voltages to an optimum value. It has been shown that such an oscillator can maintain the frequency constant for a wide range of frequencies, and that even changes in anode voltage by 50% and in heating current by 20% cause only a change of 20 cycles in 2 millions. The diagram of the circuits is given in Fig. 1.
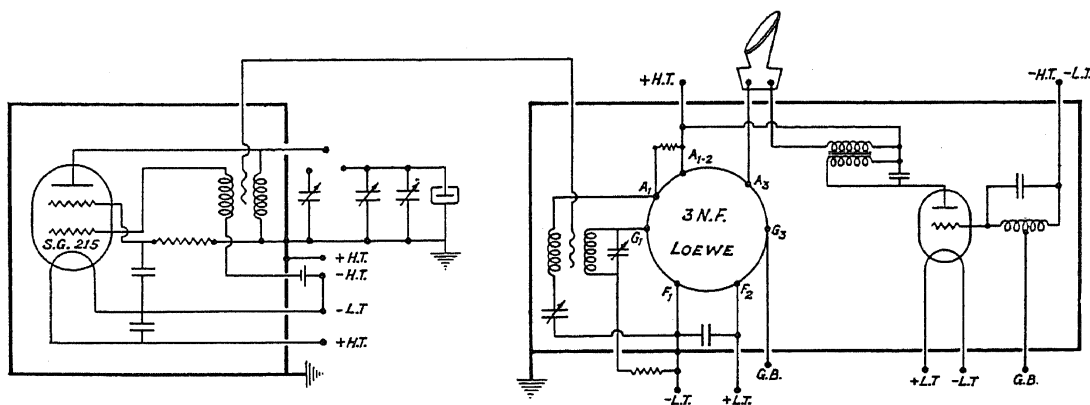

FIG. 1.

[6] L. Pauling and J. Sherman, *Jour. Chem. Phys.*, 1933, **1**, 605.
   L. Pauling, L. O. Brockway and J. Y. Beach, *Jour. Amer. Chem. Soc.*, 1935, **57**, 2705.
[7] F. Arndt and B. Eistert, *Zeit. Physik. Chem.*, (B), 1935, **31**, 125.
[8] E. C. E. Hunter and J. R. Partington, *Jour. Chem. Soc.*, 1934, 87.
   F. Arndt, G. T. O. Martin and J. R. Partington, *ibid.*, 1935, 602.
[9] M. A. Govinda Rau and B. N. Narayanaswamy, *Zeit. Physik. Chem.*, (B), 1934, **26**, 23.
[10] K. P. Schweimer and L. Pungs, *Hochfrequenztechn und Elektroak*, 1934, **43**, 181.

The beat oscillator and amplifier were built round a Loewe 3NF valve, and this together with a triode audio-frequency tuner was enclosed in one screened box. The calibrated main and vernier condensers, of capacities $1000\mu\mu F$ and $80\mu\mu F$ respectively, were arranged outside the screened-grid oscillator box, and the high tension leads were shielded by concentric tubular earthed return conductors, so as to reduce the stray capacity effects to a minimum. The constancy of the beat oscillator through the experiment was checked by switching over the screened-grid oscillator coils to an auxiliary variable condenser which was left fixed and undisturbed throughout the measurements. The apparatus worked with a remarkably constant frequency.

The densities of solutions were measured with a U-shaped dilatometer and the calculations of molecular polarisations at infinite dilution $P_{2\infty}$ at 10°, 20°, 30° and 40° C. were carried out by adopting the Hedestrand method as described already.[9]

The solvent benzene was a thiophen-free sample which was carefully dried over phosphorous pentoxide and redistilled twice in an all glass apparatus before use. All the specimens of solutes employed were "pure" as supplied by Kahlbaum and were recrystallised from distilled benzene or alcohol as the case may be, until the melting points were constant and tallied with the accepted values.

Results.

The results are given in Tables I, II and III.

TABLE I. 2·6 *Dimethyl γ-Pyrone.*

Concentration of solute in mol fraction	10°C.		20°C.		30°C.		40°C.	
	E	d	E	d	E	d	E	d
0	2·299	0·8884	2·280	0·8777	2·261	0·8669	2·242	0·8561
0·00531	2·469	0·8899	2·442	0·8792	2·415	0·8685	2·387	0·8577
0·01057	2·633	0·8913	2·598	0·8807	2·563	0·8701	2·529	0·8596
0·01108	2·640	0·8913	2·605	0·8807	2·570	0·8701	2·535	0·8596
0·01492	2·765	0·8924	2·724	0·8819	2·682	0·8713	2·641	0·8608
0·01967	2·908	0·8938	2·862	0·8833	2·816	0·8727	2·770	0·8621

	α	β	$P_{2\infty}$	$\mu \times 10^{18}$
10°	30·64	0·273	470·9	4·47
20°	29·20	0·284	459·1	4·48
30°	27·98	0·292	449·7	4·51
40°	26·64	0·307	437·8	4·51

$(P_E = 36·0)$

TABLE II. *Xanthone.*

Concentration of solute in mol fraction	10°C.		20°C.		30°C.		40°C.	
	E	d	E	d	E	d	E	d
0	2·298	0·8880	2·279	0·8773	2·260	0·8665	2·240	0·8558
0·00559	2·377	0·8918	2·354	0·8812	2·332	0·8705	2·309	0·8598
0·01024	2·443	0·8950	2·418	0·8844	2·392	0·8737	2·366	0·8630
0·01579	2·518	0·8988	2·490	0·8881	2·461	0·8775	2·433	0·8669

	α	β	$P_{2\infty}$	$\mu \times 10^{18}$
10°	13·92	0·683	244·9	2·91
20°	13·36	0·683	240·9	2·93
30°	12·77	0·699	235·5	2·94
40°	12·23	0·701	231·2	2·95

$$(P_E = 60\cdot0)$$

TABLE III. *Coumarin.*

Concentration of solute in mol fraction	10°C.		20°C.		30°C.		40°C.	
	E	d	E	d	E	d	E	d
0	2·299	0·8881	2·279	0·8774	2·260	0·8667	2·241	0·8560
0·00599	2·490	0·8909	2·462	0·8803	2·434	0·8697	2·406	0·8591
0·00918	2·590	0·8926	2·558	0·8821	2·525	0·8715	2·493	0·8609
0·01440	2·757	0·8949	2·716	0·8845	2·676	0·8740	2·635	0·8635
0·01748	2·856	0·8967	2·811	0·8861	2·766	0·8755	2·721	0·8650

	α	β	$P_{2\infty}$	$\mu \times 10^{18}$
10°	31·86	0·482	489·7	4·50
20°	30·36	0·488	477·6	4·51
30°	28·97	0·504	465·7	4·52
40°	27·45	0·514	451·4	4·52

$$(P_E = 43\cdot0 + 5\cdot5 \pm 48\cdot5)$$

The only previous determination of the moment of 2.6 dimethyl-γ-pyrone was made by Hunter and Partington,[8] but their values are considerably lower than those presented here. At 20°·0 C. the temperature at which all their measurements have been made, the $P_{2\infty}$ and moment values are 385 c.c. and 4·05 × 10^{-18} e.s.u. respectively. The value for $P_{2\infty}$ is thus lower by 74 c.c. An attempt at recalculating $P_{2\infty}$ from their published data, adopting

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the Hedestrand method, could not be carried through, as no satisfactory straight line could be drawn through the dielectric constant and density points when plotted against the molar concentration. The nearest value for a, the dielectric constant slope, was only $26 \cdot 1$ as against $29 \cdot 2$ obtained in the present experiments, and thus the difference in the values of the slope a alone accounts for 52 c.c. of the discrepancy between our results.

On account of the high moment of the molecule, the effect, on the $P_{2\infty}$ of the solute, of the decrease in dielectric constant with rise in temperature, has been noticeable, and no straight line could be drawn through the $P_{2\infty}$ points plotted against the reciprocal of the absolute temperature.[11] The same solvent effect could also be observed in the case of xanthone and coumarin.

For xanthone a moment of $3 \cdot 07$ has been reported by Bergmann and Weizmann.[12] This is in fair agreement with the present data. The value of electronic polarisation P_E used in the calculation of moment, was computed from the atomic refractivities and rounded off to $60 \cdot 0$ to take into account the atomic polarisations.

For coumarin no previous data have been reported. The P_E value has been taken from Anderlini's[13] determinations.

Discussion.

From the usual concepts of stereochemistry, and the magnitudes of the co-valency angles one should expect the pyrone-ring with its two double bonds to be a plane structure, with all the ring atoms and those directly attached to them in the same plane. As the two moment centres in the ring, the ethereal oxygen and the carbonyl group, are separated into the *para* positions, any inductive reaction between them will be negligible, and the moment of the molecule can be calculated as the difference between the two group moments as in Fig. 2.
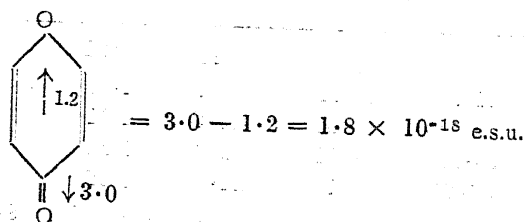
$$= 3 \cdot 0 - 1 \cdot 2 = 1 \cdot 8 \times 10^{-18} \text{ e.s.u.}$$

FIG. 2.

Now, since 2.6 dimethyl-γ-pyrone and xanthone can be regarded as symmetrically substituted γ-pyrones, their moments must be equal and have the

[11] M. A. Govinda Rau and B. N. Narayanaswamy, *Proc. Ind. Acad. Sci.*, 1935, 1, 489.

[12] E. Bergmann and A. Weizmann, *Trans. Far. Soc.*, 1936, 32, 1327.

[13] F. Anderlini, *Gazz. Chim. Ital.*, 1895, 25, ii, 142.

same value 1·8.† The observed values of 4·5 and 3·9 for these molecules are in the first instance not equal, and secondly they are both considerably higher than the calculated value. As already referred to, this has been explained as essentially due to the presence of a highly polar excited state for these molecules. The capacity of such molecules to exhibit this state is very interesting, and a regular study of this phenomenon is of great importance in elucidating the reactivities of molecules. The concept originated on the chemical side from attempts to correlate the characteristic aromatic reactions in *ortho*, *meta* and *para* substitutions, and the special properties of conjugated double bonds in transmitting polar effects. The mechanism of this change to excited states has been called by Robinson[5] electromerism, and he has given a full and connected account of these phenomena. It is a fact of general observation that when an oxygen atom is singly linked to an unsaturated carbon atom, it tends to donate one of its unshared electrons and thereby increase its co-valency with the carbon atom, the oxygen atom becoming in this process a seat of positive charge : thus
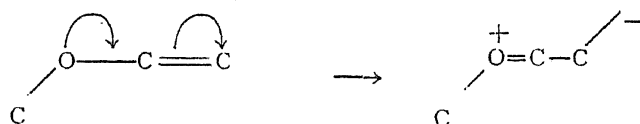
On the other hand, if the oxygen atom is doubly linked with the same carbon atom as in $- C = O$, the tendency is for the co-valency to decrease by the oxygen accepting one of the carbon electrons, and becoming a seat of negative charge : thus
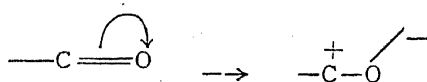
When both types of oxygen atoms are present as in the γ-pyrones, this tendency for the shift of electrons is considerably favoured and the molecule exhibits a more or less permanent displacement and therefore polarity. In the case of γ-pyrone the electromeric change is given by formula II.

I   II

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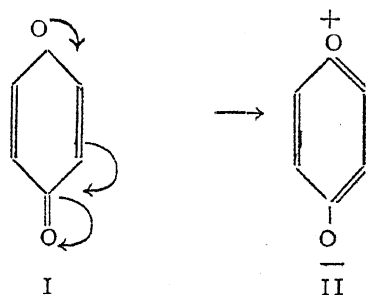
† All moment values are given in units of 10^{-18} e.s.u.

The moment of this valency isomer will be approximately
$4 \cdot 77 \times 10^{-18}$ ... $1 \cdot 5 \times 10^{-18}$ ... between neglecting the co-
valency moments. The substance is not however to be regarded as a mixture
of these two types of molecules existing in dynamic isomerism; on the other
hand, every molecule is in the identical state, intermediate between the two
extremes. Indeed, the moment of such a molecule is not the mean square
of the moments of the various unperturbed states, with a value numerically
between, but is always a vectorial mean among the values. Thus if the moment
of the excited state is in the opposite sense to that in the normal molecule,
the actual moment of the molecule will be lower than that calculated for the
normal state. These conceptions of electron degeneracy in conjugated
systems have been studied by Pauling[6] from the view-point of quantum
mechanics and he has shown that such molecules exist in a state of resonance
between two or more valence bond structures, each structure having a definite
contribution to make towards the actual state of the molecule. Thus if a
molecule can be represented by $\psi = a_1\psi_1 + a_2\psi_2$, where $a_1^2 + a_2^2 = 1$, and
a_1 and a_2 are the coefficients for the excited states ψ_1 and ψ_2, and if the
moments of these parent states along the x-axis are μ_{1x} and μ_{2x}, respectively,
then the moment of the hybrid state along this axis will be[14]

$$\mu_x = e \int \psi^* \left(\sum_i x_i - a \right) \psi \, d\tau$$

$$= a_1^2 \mu_{1x} + a_2^2 \mu_{2x} + 2 a_1 a_2 e \int \psi_1^* \left(\sum_i x_i - a \right) \psi_2 \, d\tau$$

Here e is the electronic charge, a the x-coordinate of the centroid of
positive charge, and the suffix i refers to the ith electron, there being n in
all. In this expression for the moment the third term is a cross term, which
though not negligible, is probably considerably less than the sum of the
first two terms. Accordingly we may form a rough idea of the coefficients of
the structures, if we know only the three moments. In the case of dimethyl
γ-pyrone, assuming but a single excited state with $\mu = 22 \cdot 0$, the moment
being in the same direction as in the normal co-valent molecule, a simple
calculation gives the contribution of the excited state to the moment of the
molecule to be 15%. However, such simple calculations cannot always be
carried out as the moments of the excited states may be in several different
directions and vectorial methods must then be used.

[14] L. E. Sutton, *Trans. Far. Soc.*, 1934, 30, 793.

In the case of xanthone with two benzene rings fused on to the pyrone nucleus, there are more than one of these " non-orthogonal excited canonical states " possible, each with a high moment value as in III and IV
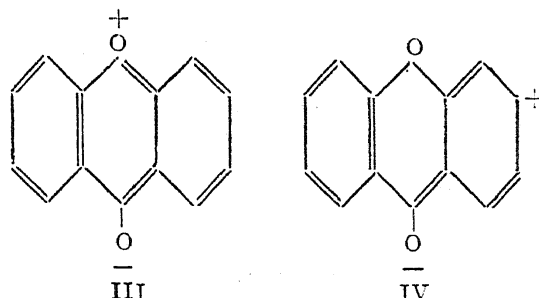
but, in addition to these, there are also a number of unexcited canonical states such as V and VI, each with the low co-valency dipole moment value of 1·8
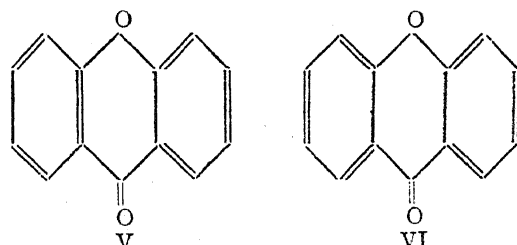
units. The presence of these latter will tend to diminish the contribution of the excited states. The moment of xanthone is therefore less than that of γ-pyrone. The moment of chromone, which is benzo-γ-pyrone, has not yet been determined, but its value must be between those of dimethyl-γ-pyrone and xanthone, if only because of the fewer number of unexcited states contributing to the resonant state than in xanthone. The observed smaller dipole moment of 2.6-diphenyl-γ-pyrone,[15] *viz.*, 3·82, could also be explained on exactly similar grounds.

The dipole moment of coumarin is another highly interesting value.[16] For the normal co-valent structure of coumarin, assuming the usual values for the group moments of $\diagup O \diagdown$ and C = O, the calculated value for the moment is 4·04 units ; see Fig. (3).
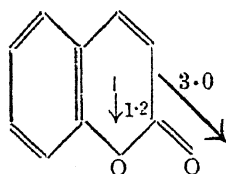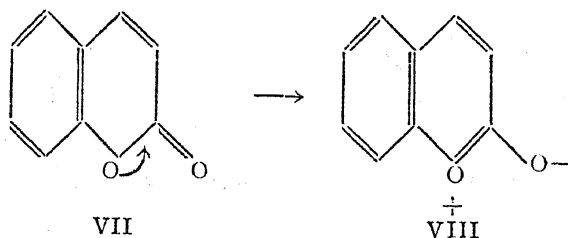

FIG. 3.

This value is only 0·5 units below the observed value of 4·5. On the theory

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15 E. C. E. Hunter and J. R. Partington, *Jour. Chem. Soc.*, 1934, 87.

16 M. A. Govinda Rau, *Curr. Science*, 1936, 5, 132.

of electromerism, there will be in coumarin also a drift of electron from the $\diagup O \diagdown$ to $C = O$, as indicated in Formula VII, leading to an excited state VIII.

VII   VIII

The approximate moment for this excited state calculated with the usual interatomic distances will be 13×10^{-18}. This smaller value for the moment of the excited state may partly account for the low increment of the observed moment value over the calculated, but only partly. For though there are here only two unexcited canonical states possible, it is interesting to observe that some of the different excited structures will have their moments in the opposite sense to that in VIII, as in IX and X

IX   X
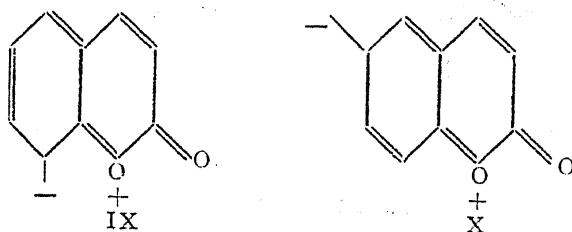
The contribution of the most prominent excited state VIII will thereby be diminished and the net contribution of the excited states will be only a small factor.

As in the case of directed substitutions in the benzene ring, the excited phases of these molecules are mainly responsible for the types of substitutions in them, and the reactivities of the groups present. A more detailed study of the moments, and their exact orientations in these molecules is called for, before a complete analysis into the various component resonating structures could be made so as to lead to more quantitative conceptions regarding the reactivities of these molecules.

Summary.

(1) The moments of 2·6 dimethyl-γ-pyrone, xanthone, and coumarin have been determined in benzene solutions at 10°, 20°, 30° and 40° C. The values for 20° are 4·48, 2·93 and 4·51 respectively.

(2) The high moments for these pyrones are due to the state of resonance in which they exist, between the unexcited states of low moments and excited states of high moments.

(3)   The difference in value between the moments of dimethyl-γ-pyrone and xanthone must be due to the greater number of unexcited parent states for the latter.

(4)   The small difference between the calculated and observed moments for coumarin is due to the moments of some of the excited phases being in the opposite sense to the normal value.