227. *The Moments of Coumarin and its 3-Phenyl Derivative and of Certain Substituted γ-Pyrones.*

By C. G. Le Fèvre and R. J. W. Le Fèvre.

The dipole moments of a number of substances related to α- and γ-pyrones are now recorded. The only previous measurements in this class were made by Hunter and Partington (J., 1933, 87), who reported a slightly lower moment for dimethylpyrone than that now found by us. Recently, however, Govinda Rau (*Proc. Indian Acad. Sci.*, 1936, *A*, **4**, 687) has published data for both this compound and coumarin, which we also had under investigation. His observations and ours are in substantial agreement in both cases.

A table of the present and past results is given below beneath the customary headings :

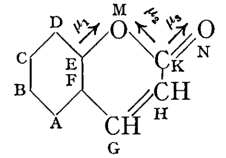
	Substance.	${}_{E}P + {}_{A}P$, c.c.	${}_{T}P$, c.c.	Temp.	μ.*	Authors.
I.	Coumarin	42	457	25°	$4{\cdot}4_8$	Le F. & Le F.
		48·5	477·6	20	$4{\cdot}5_1$	G. R.
II.	3-Phenylcoumarin	69	451	25	$4{\cdot}3_0$	Le F. & Le F.
III.	2 : 6-Dimethyl-γ-pyrone	34	480	25	$4{\cdot}6_5$	,, ,,
		35	385	20	$4{\cdot}0_5$	H. & P.
		36	459·1	20	$4{\cdot}4_8$	G. R.
IV.	3 : 5-Diacetyl-2 : 6-dimethyl-γ-pyrone	53	394	25	$4{\cdot}0_6$	Le F. & Le F.
V.	2 : 6-Diphenyl-3 : 5-dimethyltetrahydro-γ-pyrone	84	151	25	$1{\cdot}8_0$	,, ,,
VI.	Dehydracetic acid	44	210	25	$2{\cdot}8_3$	,, ,,
VII.	2 : 6-Diphenyl-γ-pyrone	72	380	20	$3{\cdot}8_2$	H. & P.
VIII.	Xanthone	57	257	25	$3{\cdot}1_1$	Le F. & Le F.†
		60	240·9	20	$2{\cdot}9_3$	G. R.

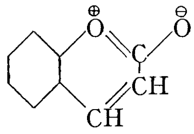
* Moments, here and throughout, are expressed in Debye units.

† This vol., p. 196.

Coumarin and 3-*Phenylcoumarin.*—The two chief moments in these molecules are those of the $\mathrm{C}\diagup\overset{}{\mathrm{O}}\diagdown\mathrm{C}$ and the C═O units. These (1 and 2·3 respectively) interact at *ca.* 60° and should, therefore, produce a resultant of about 2·9 roughly 17° anticlockwise to the axis of the carbonyl group in (I). Actually, however, the observed moments are considerably higher. This difference can very largely be attributed to intramolecular electrostatic induction, an estimation of which for the two compounds has been made by the method described by us (this vol., p. 196). For (I) we have adopted a model (see I) with the following specification : Bonds AB, BC, CD, DE, EF, KM, ME, and FA, 1·42 A.; FG,

(I.)





(I*a*.)

1·49 A. (cf. phthalocyanine, Robertson and Woodward, this vol., p. 219; diphenyl, Clark and Pickett, *J. Amer. Chem. Soc.*, 1931, **53**, 167, 3820); GH and KN, 1·32 A. (cf. benzoquinone, *Proc. Roy. Soc.*, 1934, **146**, 106, 473; *Nature*, 1934, **134**, 138); HK, 1·5 A. The points of action of the principal dipoles were taken to be the mid-points between the centres of the carbon and oxygen atoms in each case, the values being 1·01, 1·01, and 2·3 units for μ_1, μ_2, and μ_3 respectively, directed along the interatomic links as indicated on the diagram. The polarisabilities at the various atomic centres are stated in our previous paper. In the present case, however, EM and KN being only 1½° from parallel, the calculations were simplified by ignoring this slight divergence and regarding the directions of μ_1 and μ_3 as identical.

The equations used are those of Smallwood and Herzfeld (*J. Amer. Chem. Soc.*, 1930, **52**, 1919) giving the horizontal and the vertical component (μ_x and μ_y) of the induced doublet produced in a particle of polarisability α situated *r* length units away from the primary dipole whose direction makes an angle θ with r. The $\Sigma\mu_{x+y}$ values so calculated were reduced by the factor $(\varepsilon + 2)/3\varepsilon$ as suggested by Frank (*Proc. Roy. Soc.*, 1935, *A*, **152**, 188), ε being taken as 2·4 (Le Fèvre and Le Fèvre, *loc. cit.*). The results are tabulated :

Coumarin.

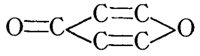
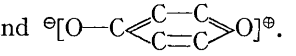
From $\mu_1\begin{cases}\Sigma\mu_x = +\,0{\cdot}50\\ \Sigma\mu_y = -\,0{\cdot}42\end{cases}$ From $\mu_2\begin{cases}\Sigma\mu_x = +\,0{\cdot}27\\ \Sigma\mu_y = +\,0{\cdot}75\end{cases}$ From $\mu_3\begin{cases}\Sigma\mu_x = +\,0{\cdot}95\\ \Sigma\mu_y = +\,0{\cdot}43\end{cases}$

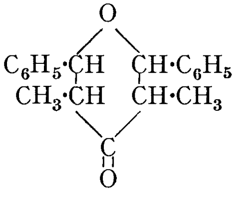
(A negative sign shows that the induced acts against the primary dipole.)

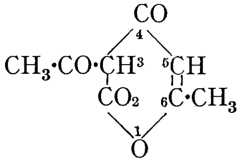
Resolution by graphical methods of the three primary and six induced component moments gave a resultant of 4·05 units acting along a direction inclined anticlockwise 15° to the axis of the C=O group and with its negative end pointing away from the molecule.

Similar treatment for 3-phenylcoumarin [on the basis of a model derived from (I) with the C–C link from H to the carbon of the substituent group 1·49 A., and with the remaining carbons separated by the normal aromatic internuclear distances] shows that at the centre of the 3-phenyl ring the total induced moments from μ_1, μ_2, and μ_3 amount to *ca.* —0·2 to —0·3 and act parallel to the C=O axis (α has been taken as $0{\cdot}9 \times 10^{-23}$ c.c., *i.e.*, the mean α for the breadth and thickness of benzene as given by Stuart and Volkmann, *Ann. Physik*, 1933, **18**, 121). This is in good agreement with experiment, by which the moment of phenylcoumarin is found to be *less* than that of its parent by approximately this amount.

In both cases the observed moment exceeds that calculated by about 0·5 unit. Following Sutton (*Trans. Faraday Soc.*, 1934, **30**, 793), this increase can be attributed to resonance between the normal molecule (I) and excited states [the chief being probably (I*a*), which corresponds to a formula proposed by Clayton (J., 1908, **93**, 524)], or, using other descriptions of the same phenomenon, to *mesomerism* (Ingold, J., 1933, 1120), or the existence of " Zwischenstufen " (Arndt and co-workers, *Ber.*, 1930, **63**, 587, 2963). (It should be noted, however, that the *idea* of permanent valency displacements occurring by the mechanism of the tautomeric effect was clearly expressed by Ingold, *Ann. Reports*, 1926, **23**, 134, 149.)

The γ-Pyrone Derivatives.—The induction occurring in the two 2 : 6-disubstituted-γ-pyrones has also been estimated, by using the appropriate dimensions listed above, but the resultant moments so calculated are several units below those found by direct measurement. It is clear, therefore, that, even more definitely than xanthone, these molecules in their real states are mesomerides between the ketonic and betaine forms :  $O{=}C\genfrac{}{}{0pt}{}{<C{=}C>}{<C{=}C>}O$ and  ${}^{\ominus}[O{-}C\genfrac{}{}{0pt}{}{<C{-}C>}{<C{=}C>}O]^{\oplus}$. Compound (V) is notable in this connection in that, owing to the absence of conjugation between the ethereal oxygen and the carbonyl group, mesomeric effects are absent and the observed moment is of the low order to be expected if the real state were practically as formulated.

(V.) 

 (VI.)

The moment found for dehydracetic acid is in agreement with structure (VI) (cf. Adams and Rassweiler, *J. Amer. Chem. Soc.*, 1924, **46**, 2758) if the 3-acetyl group is restricted in its rotation (about the bond joining it to carbon atom no. 3) to the plane dividing the molecule perpendicularly through the carbon atoms 3 and 6.

Measurements.—These were made at 25° and approximately 1200 kc. The columns contain the following data respectively : (1) the weight fraction of the solutes in the solutions, (2) the dielectric constants of the solutions, (3) their densities, (4) their specific polarisations, (6) their refractive indexes, (7) their specific refractions, and (5) and (8) the molecular polarisations and refractions of the solutes. The formula of Sugden (*Trans. Faraday Soc.*, 1933, **30**, 720) has been used in the calculations.

$w_1 \times 10^6$.	$\epsilon^{1200}_{25°}$.	$d^{25°}_{4°}$.	P_{12}.	P_1.	$n^{25°}_{D}$.	r_{12}.	$[R_L]_D$.
0	2·2725	0·87378	0·34086	—	1·49724	0·33503	
Coumarin; M = 146·1.							
11,670	2·4546	0·87698	0·37236	444·2	1·49835	0·33436	41·6
16,260	2·5305	0·87830	0·38464	443·2	1·49885	0·33422	41·7
25,039	2·6747	0·88070	0·40677	434·4	1·49979	0·33384	42·0
3-*Phenylcoumarin*; M = 222·2.							
6,044·8	2·3291	0·87552	0·35067	436·3	1·49808	0·33484	(67·5)
8,815·2	2·3538	0·87629	0·35485	428·4	1·49857	0·33483	69·4
11,463·5	2·3765	0·87690	0·35868	421·1	1·49887	0·33476	69·2
2 : 6-*Dimethyl-γ-pyrone*; M = 124·1.							
2,838·1	2·3270	0·87436	0·35075	474·8	1·49731	0·33485	33·7
3,763·5	2·3437	0·87451	0·35373	466·7	1·49731	0·33479	33·7
5,933·8	2·3853	0·87495	0·36104	464·4	1·49739	0·33467	34·0
8,213·3	2·4263	0·87546	0·36807	453·4	1·49751	0·33454	34·2
3 : 5-*Diacetyl*-2 : 6-*dimethyl-γ-pyrone*; M = 208·2.							
2,102·1	2·2910	0·87430	0·34412	393·8	—	—	—
2,712·0	2·2962	0·87446	0·34502	390·3	1·49726	0·33478	(50·6)
5,969·9	2·3248	0·87522	0·35000	389·7	1·49737	0·33455	53·0
6,054·9	2·3254	0·87525	0·35010	388·7	1·49739	0·33455	53·2
2 : 6-*Diphenyl*-3 : 5-*dimethyltetrahydro-γ-pyrone*; M = 280·3.							
6,403·1	2·2818	0·87503	0·34211	150·3	1·49773	0·33483	85·1
9,927·6	2·2870	0·87572	0·34282	150·3	1·49791	0·33467	83·7
18,832	2·2992	0·87742	0·34441	149·7	1·49842	0·33431	83·2
Dehydracetic acid; M = 168·1.							
1,110·4	2·2785	0·87410	0·34186	208·7	1·49731	0·33495	44·2
1,601·1	2·2811	0·87424	0·34229	207·4	—	—	—
2,620·8	2·2865	0·87452	0·34319	206·7	1·49742	0·33485	44·8
4,484·7	2·2962	0·87504	0·34479	204·6	1·49744	0·33466	42·5

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