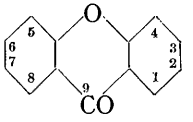
34. *The Structure of Xanthone and the Orientation of its α- and β-Dinitro-derivatives.*

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

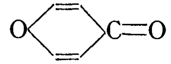

(I.)

Xanthone (I) when nitrated is converted into a mixture of α- and β-dinitro-derivatives, m. p.'s 190° and 260—262° respectively (Perkin, J., 1883, **43**, 193; Richter, *J. pr. Chem.*, 1883, **28**, 292; Graebe, *Annalen*, 1889, **254**, 286). The latter was formulated as the 2 : 7-dinitro-compound by Baeyer (*Annalen*, 1910, **372**, 138), since the dimethoxyxanthone, m. p. 180°, obtained by successive reduction, diazotisation, decomposition, and methylation, appeared to be identical with a substance synthesised from *o*-chloro-*m*-methoxybenzoic acid and quinol monomethyl ether. Le Fèvre (J., 1928, 3249) showed that α- as well as β-dinitroxanthone readily underwent hydrolytic scission by boiling piperidine, and inferred that in both compounds the nitro-groups are in positions ortho or para to the oxygen atom. The structure of the dibromoxanthone, m. p. 212°, formed by the action of bromine in acetic acid containing iodine (Dhar, J., 1916, **109**, 745), is a related question, because this compound and α- and β-dinitroxanthone, when heated with bromine in a sealed tube, all form the same (unoriented) tetrabromoxanthone.

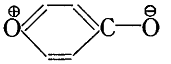
In this paper we record dipole-moment determinations on xanthone, its dibromo-, and its two dinitro-derivatives, and discuss their bearing *inter alia* on the above points. From the data tabulated later, the following results are obtained :

Substance.	Total polarisation, c.c.	Orientation polarisation, c.c.	Dipole moment, D.
Xanthone	257	200	3·11
Dibromoxanthone	421	348	4·10
α-Dinitroxanthone	253	183	2·98
β-Dinitroxanthone	747	677	5·72

Discussion.—The moment obtained for xanthone (3·11) is unexpectedly high, for by simple vector addition it should be about 1·9 (diphenyl ether and benzophenone having moments of *ca.* 1·1 and 3·0 respectively); in this particular the result recalls Hunter and Partington's observation (J., 1933, 87) that the related dimethyl- and diphenyl-γ-pyrones have moments which exceed their calculated values by 1·37 and 1·84 units. Sutton (*Trans. Faraday Soc.*, 1934, **30**, 801) considers that this exaltation arises from resonance between

(II.) 

$\mu \doteqdot 1{\cdot}9.$

 (III.)

$\mu \doteqdot 21.$

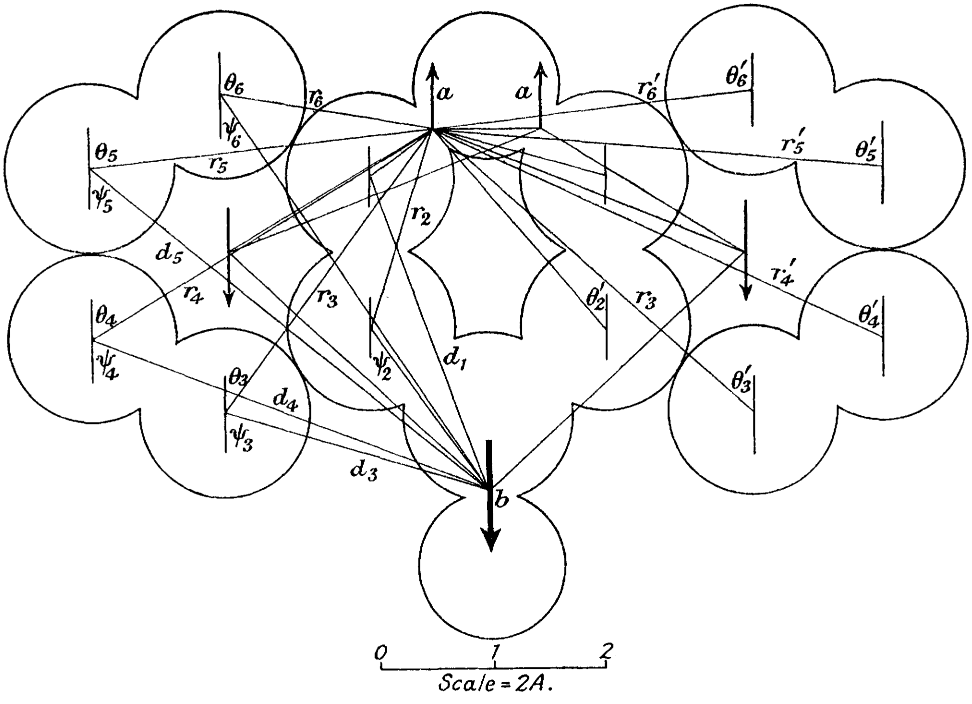
the ordinary γ-pyrone structure (II) and an excited form (III). An explanation of the present results on these lines alone would require that xanthone should possess about 10% of the character of the fully dipolar form (III). This does not seem to be the case, since it lacks the typical reactivity of the γ-pyrones, which (*e.g.*, in the 1 : 5-addition of methyl iodide or the Grignard reagent) frequently implies a facile polarisability towards (III).

More probably the observed dipole moments of these substances arise as much from intramolecular electrostatic induction processes as from mesomerism.

An attempt to estimate these contributions in the case of xanthone will be described in detail, the accompanying scale drawing serving as a basis for the calculation. The assumption has been made that the central ring has the γ-pyrone structure; the attached aromatic nuclei accordingly correspond to one of the Kekulé forms. Evidence for this is discussed later in this paper. The double and single bond lengths used are 1·32 and 1·52 A. respectively, and the radius of oxygen 0·66 A.

The method involves the calculation and algebraical summation of the various fractional moments (μ_x) induced by the principal moments parallel to the O–CO axis. One requires, therefore, various distances and angles; these are obtained accurately enough from the diagram. (It is noteworthy that they are not greatly different for a model in which the aromatic rings are regular hexagons with benzenoid internuclear distances and the oxygen and ketonic valency angles of the order 120°.)

The general equation for the induced moment in a medium of dielectric constant unity is $\mu_x = \alpha\mu(3\cos^2\theta - 1)/r^3$, in which α is the polarisability at a point r A. from the seat of the inducing doublet (considered as the point of contact of the two atoms composing the polar link), and θ is the angle between r and the vertical (O–CO) direction. The link moments adopted have been: C–O, 0·9; C=O, 2·5 (Sidgwick, "The Covalent Link in Chemistry," 1933, 153). We have further assumed that the radius of carbonyl carbon equals that of carbon doubly linked to carbon; this is not unreasonable, since the chemistry of the ketone group indicates that the carbon definitely tends to be electrically positive, and elements as kations have smaller radii than when linked to other atoms by bonds of low polarity. This simplifies the calculation, because the upward component of each ether link (*a*) therefore becomes 0·9 cos 52·5°. The total vertical moment due to the ethereal oxygen and acting against the CO moment (*b*) is twice this, *viz.*, 1·10. Each of these three components will induce moments (μ_x) in the various polarisable parts of the molecule. Only those lying in directions parallel to the vertical need be computed, however, since those at right angles are in symmetrically opposed pairs and therefore mutually cancel in the resultant.



In similar calculations for certain diphenyl compounds (J., 1936, 1130) we considered the polarisability of benzene in its plane as effectively situated at the mass centre.* It might, however, be urged that this assumption is only permissible when the benzene ring is several Ångstrom units distant from the primary dipoles. In the molecule under consideration, the latter are directly attached to the rings and the induced dipoles should vary markedly in sign and magnitude on each of the carbon atoms. These have, therefore, been

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* If this is done in the present case, we find (taking $\alpha = 1{\cdot}24 \times 10^{-23}$ e.s.u.; Stuart and Volkmann, *Ann. Physik*, 1933, **18**, 121) the resultant calculated induced moment to be −1·68, *i.e.*, 0·4 lower than that obtained by the more detailed calculation.

calculated separately. The polarisabilities of the carbon atoms and of the CH units have been taken as the same, *viz.*, $2\cdot05 \times 10^{-24}$ e.s.u., and have been located at the centres of the carbon atoms. The results and the data upon which they are based are set out below. The distances from the point of action of each of the C–O dipoles to the centres of the carbon atoms in the nearer ring are r_1, r_2, etc., and to the corresponding carbon atoms of the more distant ring, r_1', r_2', etc. The angles which these lines make with the vertical are θ_1, θ_2, . . . , θ_1', θ_2' . . . etc., respectively. The corresponding values for the case of the ketonic dipole are d_1, d_2, d_3 . . . , and ψ_1, ψ_2, ψ_3 . . . , etc. As far as possible, the data are shown in the diagram.

r_2	$1\cdot8_6$	θ_2	17°	μ_{x2}	$+0\cdot3_0$	$r_{1'}$	$1\cdot5_8$	$\theta_{1'}$	75°	μ_{x1}'	$-0\cdot2_3$
r_3	$3\cdot1_2$	θ_3	37°	μ_{x3}	$+0\cdot0_3$	$r_{2'}$	$2\cdot3_8$	$\theta_{2'}$	41°	μ_{x2}'	$+0\cdot0_6$
r_4	$3\cdot5_5$	θ_4	59°	μ_{x4}	$-0\cdot0_1$	$r_{3'}$	$3\cdot8_5$	$\theta_{3'}$	49°	μ_{x3}'	$+0\cdot0_0$
r_5	$3\cdot0_0$	θ_5	85°	μ_{x5}	$-0\cdot0_4$	$r_{4'}$	$4\cdot4_0$	$\theta_{4'}$	65°	μ_{x4}'	$-0\cdot0_1$
r_6	$1\cdot9_0$	θ_6	100°	μ_{x6}	$-0\cdot1_5$	$r_{5'}$	$4\cdot0_2$	$\theta_{5'}$	86°	μ_{x5}'	$-0\cdot0_2$
						$r_{6'}$	$2\cdot8_5$	$\theta_{6'}$	96°	μ_{x6}'	$-0\cdot0_5$
d_1	$3\cdot0_0$	ψ_1	20°	μ_{x1}''	$-0\cdot3_2$	d_4	$3\cdot7_8$	ψ_4	69°	μ_{x4}''	$+0\cdot0_6$
d_2	$1\cdot8_0$	ψ_2	36°	μ_{x2}''	$-0\cdot8_5$	d_5	$4\cdot5_5$	ψ_5	51°	μ_{x5}''	$-0\cdot0_1$
d_3	$2\cdot4_5$	ψ_3	73°	μ_{x3}''	$+0\cdot2_5$	d_6	$4\cdot2_4$	ψ_6	33°	μ_{x6}''	$-0\cdot0_8$

In addition there are the effects of the ketonic group on the ethereal oxygen and *vice versa* to be considered. From the atom refractions (Na line) of carbon, carbonyl oxygen, and ethereal oxygen (2·418, 2·211, 1·643), the respective average polarisabilities are calculable as 0·09, 0·09, and $0\cdot07 \times 10^{-23}$. By taking the appropriate distances from the diagram, it is found that the interaction between the ethereal linkages and the carbon and the oxygen of the carbonyl group causes induction of + 0·11 and + 0·03, and the effect of the ketonic radical on the oxygen atom induces — 0·08 on the latter.

When the last results are added to $2\Sigma\alpha\mu(3\cos^2\theta - 1)/r^3$ (from the above tables) a resultant of —2·08 units is obtained. The *actual* induced resultant moment will, however, be $(\varepsilon + 2)/3\varepsilon$ times less than this, ε being the dielectric constant of the internuclear space. The order of ε should be derivable from measurements of the rate of variation of the dielectric constant of benzene under increasingly high pressures, *i.e.*, when the internuclear space is diminishing. The limiting value should be the quantity required in our calculation.

Ortvay (*Ann. Physik*, 1911, **36**, 14) found that, for several liquids, dielectric constant and pressure were connected by a quadratic relation: $\varepsilon_p = \varepsilon_0(1 + \alpha p + \beta p^2)$, where $\varepsilon_p - \varepsilon_0$ is the dielectric constant change for a pressure increase of p kg./cm.². From this equation the pressure at which ε_p becomes constant is $-\alpha/2\beta$, and since for benzene $\alpha.10^4 = 0\cdot603$ and $-\beta.10^7 = 0\cdot164$, the maximum value of the dielectric constant at 25° is $2\cdot273 \times 1\cdot055 = 2\cdot40$. Adopting the Clausius–Mosotti model, therefore, we estimate that the induction in the xanthone molecule should be reduced by 4·4/7·2. It accordingly becomes — 1·16 units.

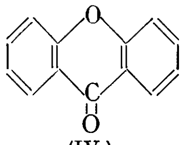
Conclusions.—The observed dipole moment of xanthone (— $3\cdot1_1$) can be considered to arise from the vectorial addition of (*a*) the bond moments (+ 1·1 — 2·5), (*b*) the induced moments (— $1\cdot1_6$), and (*c*) a "mesomeric" moment ($0\cdot5_5$). The smallness of the last indicates that a form containing the pyrone unit as in (III) can only make *ca.* 3% contribution to the real structure.

Fixation of Links.—Further information concerning the structure of xanthone is derivable from the moments found for dibromo- and for β-dinitro-xanthone. From the general order of these results the substituents are clearly in the positions 2 : 7; further (see p. 196), an independent chemical proof has been provided for the constitution of the second compound. If now we take the moment due to bromine to be 1·5 and that due to nitroxyl to be 4·0 and attribute the excess of the moment of each compound over that of xanthone to the two Br and the two NO_2 component moments in each case, it is seen that the two bromines constitute a resultant of 1·0 and the two nitro-groups one of 2·61. Application of the well-known formula for vector addition of dipole moments shows that in the two cases the individual moments lie along directions making angles with one another of 141° and 142° respectively.

In view of the possibility that the values taken above for the component moments may be slightly too small (owing to the interactions between the 2 : 7-dipolar groups and the oxygen atom and the ketonic radical of the central ring) it is important to note the direction in which the error in the above calculation will lie. If m be the component moments and θ be the angle at which they act, then we have : $\cos\theta = [(\text{Resultant})^2 - 2m^2]/2m^2$. From the order of the figures above, $\cos\theta$ is negative; obviously therefore any *increase* on the value of m will cause θ to approach the limiting value, *viz.*, 180°. Thus our calculation of the amount of widening of the 2 : 7-valency angles is a minimum estimate, and our explanation would be strengthened rather than weakened by the adoption of the more correct values, if they were obtainable, for μ_{Br} and μ_{NO_2} in these compounds.

An estimate of the degree of induction by the nitro-group on the ethereal oxygen is easily made. The distance from the centre of the oxygen atom to the point of contact of the nitrogen and carbon atoms in either the 2 or the 7 position is *ca.* 5 A. The polarisability of an ethereal oxygen atom is $0{\cdot}07 \times 10^{-23}$ e.s.u., and if the moment of the inducing dipole is taken as 4 (*i.e.*, the value for nitrobenzene), μ_{induced} becomes $2\alpha\mu.10^{-17}/r^3 = 0{\cdot}04 \times 10^{-18}$. Such an increase scarcely affects the value of $\cos\theta$. Since, however, Sutton and Hampson (*Trans. Faraday Soc.*, 1935, **31**, 945) find that in 4-nitrodiphenyl ether considerably greater interaction moments may be operative, we will observe that if, in the case of 2:7-dinitroxanthone above, the nitro-component moment were 4·5, $\cos\theta$ would be $-0{\cdot}8318$, and θ only 147°.

Our present results are in agreement with (IV), in which the two C–X bonds would most probably be inclined at an angle of the order 140°. The cause which could underlie the development of such a structure has been discussed by Mills and Nixon (J., 1930, 2510) : for geometrical reasons the angles between the double bond and each of the single links in $C_1{=}C_2{<}^{A}_{B}$ will be *ca.* 125° if the angle A–C_2–B has the normal tetrahedral value, *viz.*, 110°. Therefore in a stabilised Kekulé benzene structure there will be an alternation of angles between successive pairs of the external C–H valencies. But since the hexagonal angle in aromatic compounds is 120°, the angle C_1–C_2–B of the above unit must, in the construction of the benzene nucleus, become reduced by 5°. Thus the two external angles will together make 240°. This is all that can definitely be said regarding their values. A reasonable guess is that the strain is divided more or less equally, giving angles of *ca.* 127½° and 112½°. Our results correspond to 130° and 110°. They are therefore in accord with the theoretical prediction of Mills and Nixon (*loc. cit.*) that fusion of a benzene ring with a 6-membered ring tends towards the stabilisation in the former of that Kekulé individual which has a double bond *between* the points of attachment of the side nucleus. To a small extent the observed splaying of the 2 : 7-valency directions may be caused by the differences between the radii of the ethereal oxygen and the ketonic carbon atom in the γ-pyrone nucleus; for the reasons noted above, however, this is probably very slight. We have neglected it in the discussion of α-dinitroxanthone (later), and take the view that if the side rings of xanthone were fully mobile—*e.g.*, as in benzene itself—we should have found, instead of an angle of *ca.* 140°, one of *ca.* 120°.



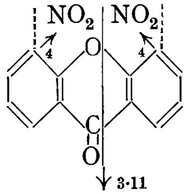
(IV.)

An implication of the present conclusions is that both the oxygen and the ketonic valency angles must in these substances be approximately 100°. For the former, such a result is not necessarily abnormal, since values between 90° and 180° have been reported to occur in different compounds (cf. Bernal, *Trans. Faraday Soc.*, 1934, **30**, 860; Bennett, *ibid.*, p. 853; Hampson and Sutton, *Proc. Roy. Soc.*, 1933, *A*, **140**, 562; Hampson, Farmer, and Sutton, *ibid.*, 1933, *A*, **143**, 158). The ketonic angle has not been so fully discussed (cf., however, LeFèvre and LeFèvre, J., 1935, 1701), but it is evidently also easily influenced by, *e.g.*, spatial requirements of attached groups. In most compounds it appears to have an angle of 110° ± 5° (Dornte, *J. Amer. Chem. Soc.*, 1933, **55**, 4126), but in some (*e.g.*, linear carbon suboxide, LeFèvre and LeFèvre, *loc. cit.*) this is presumably vanishingly small, and in others (*e.g.*, dimeric keten and tetramethyl*cyclo*butanedione, cf. J., 1935, 1751) it must approach 90°.

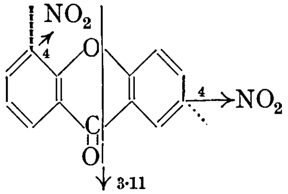
An implied reduction of the ketonic valency angle, therefore, does not invalidate *a priori* the present conclusions. Hence, dinitro- and dibromo-xanthones constitute cases additional to those recently presented by Sidgwick and Springall (J., 1936, 1532) in which physical measurements clearly show the fixation of the conjugated linkings of an aromatic ring system.

Relation of Xanthone to Diphenyl Ether and Benzophenone.—If the xanthone molecule is regarded as benzophenone and diphenyl ether superimposed, it might at first appear that the moment of xanthone should accurately equal the difference between those of the other two compounds, since in the *experimental* values for these the effects of induction are included incidentally. As stated previously, however, such a method of calculation gives a result 1·2 units too small. Three causes may be suggested for this: (1) The benzene rings in the free molecules of diphenyl ether and benzophenone are undoubtedly in a state of oscillation and rotation; in xanthone they are tied into a flat configuration—thus, since benzene is more polarisable in its plane than in other directions, induction processes will proceed farther in xanthone than in the separate molecules named. (2) The oxygen and carbonyl valency angles are probably greater in diphenyl ether and benzophenone than in xanthone; thus in the latter compound the polarisable benzo-nuclei are more behind the inducing dipoles than they are in the two separate substances; the effect of this on the induction occurs through the angle θ: the smaller θ is, the greater is $(3 \cos^2 \theta - 1)$, up to the limiting value of 2 (where $\theta = 0°$ or $180°$). Inspection of the formula used in the calculation above shows that a diminution in the angle θ corresponds to an *increase* in the induced moment. (3) The reciprocal effects between the carbonyl group and the oxygen atom should be considered. Moreover, (4) there is no certainty that in the three compounds interatomic distances are the same; since these enter the calculation as their cubes, quite slight alterations in them could materially change the magnitudes of the induced moments.

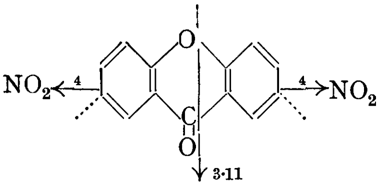
The Orientation of α-Dinitroxanthone.—Using the above results and conclusions, we have calculated the moments to be expected for each of the four possible dinitroxanthones. The values are given below their respective formulæ (V)—(VIII), the dotted lines indicating the directions the side-chain linkings would take up if the aromatic nuclei were mobile; *e.g.*, in (V) they are parallel and in (VI), (VII), and (VIII) at 120°. It is noteworthy that the change of dipole moment consequent upon the degree of valency deflection indicated by our results above—about 10°—is easily measurable. Thus if in (VII) no fixation of links were to occur, then its resultant molecular moment should be *ca.* 7. The difference between this figure and that actually found (7 — 5·8 = 1·2) corresponds to a polarisation of some 30 c.c.



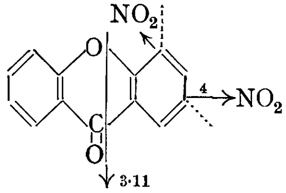
(V.) $\mu = 4·78$.



(VI.) $\mu = 4·49$.



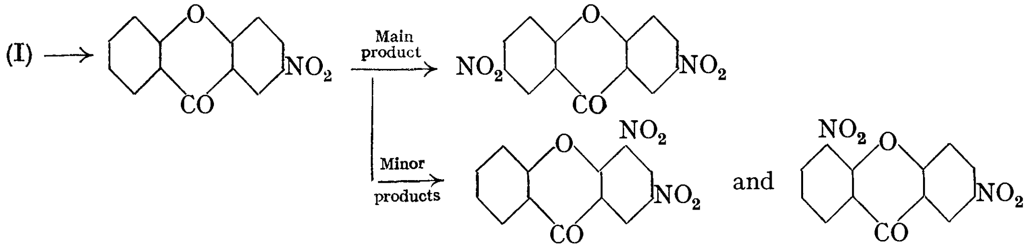
(VII.) $\mu = 5·84$.



(VIII.) $\mu = 3·11$.

The observed moment of α-dinitroxanthone is 2·98. It would therefore appear to be the 2 : 4-compound. A substance of this structure has been synthesised from 2 : 4-dinitro-2′-carboxydiphenyl ether (Ullmann, *Annalen*, 1909, **366**, 87), but it has a higher m. p. (206°), although in appearance, solubility, etc., it shows a strong resemblance to α-dinitroxanthone, m. p. 190°. The latter preparation, upon further examination, behaved as a difficultly separable mixture. Recrystallisation from chloroform or benzene gradually raised the m. p.

from *ca.* 190° to *ca.* 198°, but even then the substance, although analytically pure and conforming to the descriptions given in the literature, had not the well-defined crystalline appearance usually associated with chemical homogeneity. The progress of the purification was followed by carrying out density and dielectric-constant measurements on benzene solutions of each batch. The polarisations (and therefore the apparent moments of the " α-dinitroxanthone ") decreased with increase of m. p. down to the value now recorded for the α-dinitro-compound. The impurity being removed was therefore of higher polarity, probably either (VI) or (VII); according to this view the nitration of xanthone proceeds thus :



EXPERIMENTAL.

Preparation of Substances.—Xanthone is not readily attacked by nitric acid or the halogens. Perkin (*loc. cit.*) and Richter (*loc. cit.*) dissolved the substance in mixed acids and left the solution for several hours; the chief product was then the β-dinitro-derivative, which after purification had reported m. p.'s from 260° to 262°. From the mother-liquors obtained in the crystallisation, the α-compound was isolated first by Richter, who gave the m. p. as 145—150°, but later, Graebe (*loc. cit.*) found 190°. According to the latter, xanthone and cold fuming nitric acid when left together for several days yield only the α-dinitro-derivative, apart from unchanged xanthone.

In the present work a number of unsuccessful attempts were made to mononitrate xanthone. The methods applied (potassium nitrate and sulphuric acid; nitric and acetic acids) led to the isolation of impure dinitroxanthones mixed with unattacked material. The preparations of β-dibromo- and β-dinitro-xanthone were carried out according to the directions of Dhar (J., 1916, **109**, 747). The dibromo-compound was recrystallised from absolute alcohol and had m. p. 212—213° (Found : C, 44·0; H, 1·8. Calc. : C, 44·1; H, 1·7%); β-dinitroxanthone, crystallised from chloroform, had m. p. 261—262° (Found : C, 54·6; H, 2·2. Calc. : C, 54·5; H, 2·1%).

α-Dinitroxanthone.—Xanthone (5 g.) was added to nitric acid (*d* 1·5; 50 c.c.) at 0°, and the solution left at room temperature for 4 days. Dilution, filtration, thorough washing with boiling water, and drying at 100° then afforded a white powder (*ca.* 7 g.) which softened at about 180° and was liquid by 187° (Found : C, 55·0; H, 2·3%). Admixture with β-dinitro- or 2 : 4-dinitroxanthones was without ascertainable effect on this m. p.

This crude material, examined in benzene solution, showed an apparent polarisation of the order 350 c.c., corresponding to a moment of 3—4 units. Repeated recrystallisation from much chloroform finally produced a small quantity of yellow crystalline material, m. p. 196—198°, which also showed an indefinite mixed m.p. behaviour (Found : C, 54·3; H, 2·3%). The measurements recorded in detail were made on this sample.

Observations.—In the accompanying tables the symbols have the following significances : f_1, the molar fraction of the solute in each solution; d, the density of the solution compared with

$f_1 \times 10^6$.	ϵ.	d.	P_{12}.	P_1.
		Benzene.		
0	2·2725	0·87380	26·5863	—
		Xanthone.		
447·64	2·2790	0·87410	26·6905	259·4
800·11	2·2836	0·87433	26·7649	249·8
933·26	2·2851	0·87441	26·7897	244·5
1121·5	2·2877	0·87453	26·8316	245·3
		β-Dibromoxanthone.		
401·15	2·2832	0·87462	26·7558	449·2
1259·05	2·3036	0·87650	27·0760	415·6
2001·1	2·3211	0·87814	27·3486	407·7
2615·5	2·3351	0·87948	27·5667	401·4

$f_1 \times 10^6$.	ϵ.	d.	P_{12}.	P_1.
		α-Dinitroxanthone.		
94·20	2·2738	0·87394	26·6078	254·8
117·51	2·2741	0·87398	26·6126	250·2
237·18	2·2758	0·87416	26·6406	255·5
279·95	2·2763	0·87423	26·6488	249·7
		β-Dinitroxanthone.		
100·85	2·2772	0·87391	26·6590	747·6
111·60	2·2777	0·87392	26·6668	748·2
178·22	2·2808	0·87399	26·7147	746·8
225·55	2·2829	0·87404	26·7472	740·0

water at 4°; ε, the dielectric constant of the solution at approx. 1200 kc.; P_{12} and P_1, the apparent polarisations of the solution and the solute at the stated concentrations; α and β, the coefficients of change of dielectric constant and density with reference to f_1. The solvent used was benzene throughout, and all measurements were made at 25°.

From the above data, the polarisation at infinite dilution (${}^{\infty}P_1$ in following table) of each of the four solutes has been calculated by the expression ${}^{\infty}P_1 = A(M_1 - B\beta) + C\alpha$ (cf. J. 1936, 491). For the present solvent the constants A, B, and C are respectively 0·34085, 89·265, and 14·670.

	Xanthone.	β-Dibromoxanthone.	α-Dinitroxanthone.	β-Dinitroxanthone.
Mean α	14·36	24·90	13·76	46·50
Mean β	0·6593	2·132	1·512	1·068
${}^{\infty}P_1$	257·4	421·1	253·3	747·1

SUMMARY.

The dipole moment of xanthone is found to be 3·11. The excess of this value over that calculated from diphenyl ether (*ca.* 1·0) and benzophenone (*ca.* 3·0) is largely due to electrostatic induction effects operating between different groups in the molecule. The amount of such induction is calculated. A fully dipolar form ($\mu = ca.\ 21$) cannot make more than a 3% contribution to the real structure.

The observed moments of two 2 : 7-disubstituted xanthones show that the links holding the substituents in each case are at 141—142° to each other, *i.e.*, that a nearly complete fixation of double and single bonds occurs in the xanthone skeleton. This result is in agreement with the theory of Mills and Nixon. On this basis the moments of the four possible dinitroxanthones have been calculated. "α-Dinitroxanthone" is thereby seen to be a slightly impure specimen of 2 : 4-dinitroxanthone.

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