339. *Evidence for a Skew Structure of Benzil.*

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

The suggestion is made that the stable configuration of benzil in non-polar solvents is one in which the ketonic groups, with their appropriate bonds, are effectively situated in, or make rotational oscillations of low amplitude about, two planes which are roughly mutually perpendicular (as illustrated in Fig. 2).

The evidence consists in the value of the dipole moment of benzil, the fact that this shows no greater dependence upon solvent than does the corresponding value for phenanthraquinone, and the observations that the moment is constant throughout a temperature range of 65° in decalin, or 25° in benzene or carbon tetrachloride.

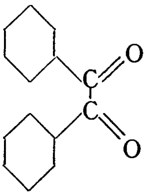
Other explanations of these data are discussed and rejected.

Such a " skew " structure could arise if the dominant forces setting the shape of the molecule were superimposed dipolar repulsions between the C=O moments and steric repulsions between the phenyl groups and oxygen atoms (tending to a *trans*-structure) and van der Waals attractions between the phenyl groups (tending to a *cis*-structure). Compatibly with such a view diacetyl (in which dipolar repulsions should be much the same as, but the van der Waals attractions weaker than, in benzil) appears to be either much more flexible or more *trans* in type.

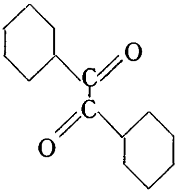
In recent years the configurations and resultant polarities of organic molecules in which inner rotation of dipolar groups can occur have received general theoretical treatment by Williams (*Z. physikal. Chem.*, 1928, *A*, **138**, 75), Meyer (*ibid.*, 1930, *B*, **8**, 27), Smyth, Dornte, and Wilson (*J. Amer. Chem. Soc.*, 1931, **53**, 4242), Zahn (*Physical Rev.*, 1931, **38**, 521; 1932, **40**, 291), Greene and Williams (*ibid.*, 1932, **42**, 119), Smyth and Kamerling (*J. Amer. Chem. Soc.*, 1932, **53**, 2988), Lennard-Jones and Pike (*Trans. Faraday Soc.*, 1934, **30**, 830), Penney and Sutherland (*ibid.*, p. 898), Altar (*J. Chem. Physics*, 1935, **3**, 460), Hampson and Weissberger (*J. Amer. Chem. Soc.*, 1936, **58**, 2111), and others. The cases most studied experimentally have been the *s*.-dihalogenoethanes, for which it appears that at ordinary temperatures and in dilute solution or the vapour state the majority of the molecules are exhibiting rotational oscillations of fairly large amplitudes. The apparent moments increase with rise of temperature, showing that the non-polar *trans*-

form is the one with minimum potential energy, and suggesting that the predominant forces determining the configuration are electrostatic in type. With hydrogen peroxide, hydrazine, and certain disubstituted diphenyl compounds other factors, such as the interactions of electron clouds in adjacent atoms (Penney and Sutherland) or London forces (Hampson and Weissberger) or steric effects (various authors) have been supposed to be simultaneously operative in producing specified structures; but it should be mentioned that the experimental results against which such *a priori* discussions have been checked are limited to a small number obtained with solutions and liable therefore to uncertainties arising from the superposition of at least two causes, which we have tried to avoid in the present work: (1) the usual solvent-polarisation dependence found to a greater or less degree in all solution measurements of dipole moments, and (2) alterations of the configuration due to solvent influences upon each of the two polar rotatable halves of the molecule and their mutual electrical and other interactions.

This paper deals with the case of benzil, a molecule which can assume any configuration between the two extremes (I) and (II). These will be characterised by a high moment and no moment respectively. The polarity of (I) could be estimated from a knowledge of the C = O group moment by a calculation such as that employed, *e.g.*, for xanthone (cf. J., 1937, 196), but as this would involve certain speculative quantities, it is probably much safer to adopt for (I) the value now found for phenanthraquinone (III), *viz.*, 5·6, a figure in which induction processes, etc., are automatically included. The apparent dipole moments which benzil shows in different solvents are, however, intermediate between the extremes 0 and 5·6. They are listed in Table I, and show a variation between themselves from $3{\cdot}7_8$ in dioxan to $3{\cdot}2_1$ in chloroform. To assess the extent to which this is due to configurational changes in the benzil molecules, measurements have also been made on phenanthraquinone in benzene, carbon disulphide, dioxan, and chloroform (sparing solubility precluded a wider selection of solvents). These data (see Table I) are likewise not independent of the solvent; but as phenanthraquinone, unlike benzil, is presumably a rigid molecule, these variations can be due only to "normal" solvation effects. This inference is supported by the existence of a much smoother relation between the orientation polarisations of phenanthraquinone and the dielectric constants of the solvents than between the corresponding quantities for benzil (see Fig. 1). Müller (*Trans. Faraday Soc.*, 1934, **30**, 731) has shown that in many such cases the steepness of the polarisation–dielectric constant curve depends upon the magnitude of the moment of the solute under examination; in the present work, therefore, since the moment of phenanthraquinone is greater than that of benzil, removal of the effects of solvation in the data for the latter with the aid of the



(I.)



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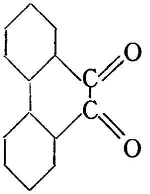


(III.)

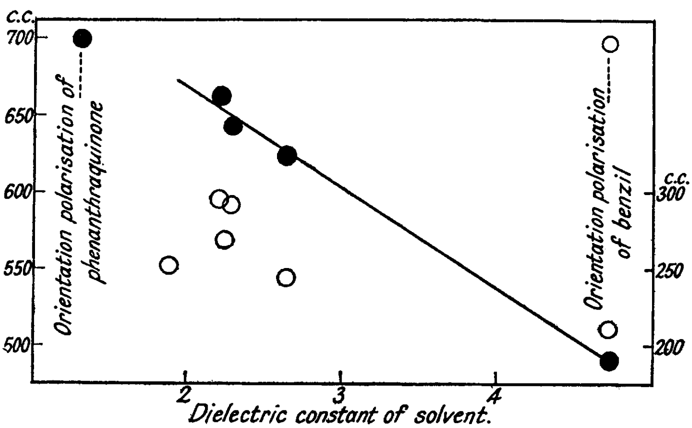
TABLE I.

Apparent Dipole Moments (μ) *and Total Polarisations* ($_{T}P$) *of Benzil, Phenanthraquinone, and Acenaphthaquinone in Various Solvents at* 25°.

Solvent.	ε of solvent.	Benzil.		Phenanthraquinone.		Acenaphthaquinone.	
		$_{T}P_\infty$.	μ.	$_{T}P_\infty$.	μ.	$_{T}P_\infty$.	μ.
n-Hexane	1·888	315	$3{\cdot}4_9$	—	—	—	—
Decalin	2·099	292	$3{\cdot}3_3$	—	—	—	—
Dioxan	2·209	358	$3{\cdot}7_8$	724	5·66	—	—
CCl_4	2·227	331	$3{\cdot}6_0$	—	—	—	—
Benzene	2·273	355	$3{\cdot}7_6$	704	$5{\cdot}5_7$	819	$6{\cdot}0_8$
CS_2	2·640	307	$3{\cdot}4_4$	686	$5{\cdot}5_0$	—	—
$CHCl_3$	4·724	274	$3{\cdot}2_1$	521	$4{\cdot}7_1$	—	—

information obtained for the former should result in over- rather than under-compensation. However, when the orientation polarisation of benzil in dioxan is reduced by the ratio of the orientation polarisations of phenanthraquinone in benzene and dioxan, and those in carbon disulphide and chloroform increased by the analogous phenanthraquinone values in these solvents, the following set of figures is obtained—comparable to the datum in benzene—in which solvation effects should have been eliminated :

FIG. 1.

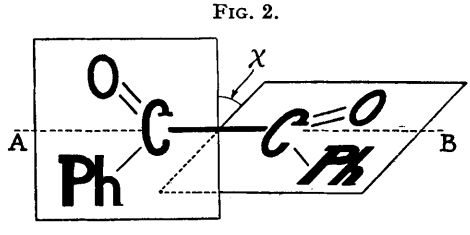


Solvent	Dioxan	Benzene	CS_2	$CHCl_3$
${}_0P$, c.c.	286	292	251	295
μ	$3{\cdot}7_2$	$3{\cdot}7_6$	$3{\cdot}4_8$	$3{\cdot}7_8$

The low value given in Table I for the moment of benzil in chloroform is therefore probably due to a solvent effect, since after correction it agrees well with that found in dioxan or benzene. On the other hand, it is evident that the lower moments found in hexane and carbon disulphide cannot have been caused mainly by solvation, for—where the comparison is complete—the action which the latter solvent has on benzil is out of proportion to that which it has on phenanthraquinone; however, it is well known that carbon disulphide has some specific and unidentified solvent action (compare, *e.g.*, Hoecker, *J. Chem. Physics*, 1937, **5**, 372).

The Configuration of Benzil.—The two equal chief components (denoted in what follows by μ) of the polarity of benzil obviously act approximately parallel to the directions of the links uniting the carbon to the oxygen atoms, and with a knowledge of their magnitude, together with the reasonable assumptions concerning valency angles embodied in Fig. 3, certain conclusions concerning the structure of benzil can be reached. In the present work a value for μ has been simply obtained by considering phenanthraquinone as a special case of Fig. 2 for which $\chi = 0°$ and the resultant moment is 5·6; therefore—since, from symmetry, whatever the value of χ the resolutes along AB of the two components always balance out, and only those perpendicular to this axis contribute to the experimentally determined resultant, so that, the central ring of phenanthraquinone being regarded as a regular hexagon—we have : $\mu = 5{\cdot}6 \div 2 \cos 30° = 3{\cdot}2_3$.

FIG. 2.



Four possibilities suggest themselves : (1) that the two halves of the benzil molecule are in completely free rotation about the central C–C bond, (2) that they are in hindered or restricted rotation, (3) that they are fixed in, or are making rotational oscillations of low amplitude about, planes making an angle $\chi°$ with one another (see Fig. 2), or (4) that a benzil solution contains a mixture of flat, completely *cis*- or *trans*-mesomerides (*i.e.*, planar forms stabilised by resonance). Our dipole-moment measurements alone would agree satisfactorily with (1), (3), or (4).

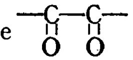
For a state of free intramolecular rotation, the resultant moment should be $\sqrt{2}\mu$ sin 60° $= 1{\cdot}4 \times 3{\cdot}2 \times 0{\cdot}87 = 3{\cdot}9$. Nevertheless, this is an unlikely occurrence, since unhindered rotation does not take place in the closely related cases of the stilbene chlorides (Ph·CHCl·CHClPh, Weissberger and Sängewald, *Z. physikal. Chem.*, 1930, **93**, 133) and the hydrobenzoins [Ph·CH(OH)·CH(OH)·Ph, Hassel and Naeshagen, *Tids. Kjemi Berg.*, 1930, **10**, 93; *Z. physikal. Chem.*, 1931, **14**, *B*, 232], for which the moments of the optically active enantiomorphic forms were found to be considerably greater than those of the corresponding optically inactive, but structurally similar, *meso*-forms. Had free rotation been possible, they would, of course, have been identical.

For a state of hindered rotation, the resultant moment might be expected from analogies with, *e.g.*, ethylene dichloride and dibromide (Müller, *Physikal. Z.*, 1933, **34**, 689; Smyth and Walls, *J. Amer. Chem. Soc.*, 1931, **53**, 2115) to be sensitive to both solvent and temperature. We have pointed out above, however, that the variation of the apparent moment of benzil from solvent to solvent beyond that which might be caused by ordinary solution effects is practically nil; moreover, in carbon tetrachloride or benzene solutions a rise of temperature of 25° causes no detectable increase in the moment, and in decalin measurements at 25°, 50°, 70°, and 90° have given values of $3{\cdot}3_3$, $3{\cdot}3_1$, $3{\cdot}3_4$, and $3{\cdot}3_4$ respectively. Hence, within the limits of experimental error, the moment is demonstrably very insensitive to temperature. This is in agreement with (3).

As to the fourth suggestion, a numerically adequate explanation of the present results could be provided were the *cis*- and the *trans*-form to occur in approximately equal proportions. This is, however, probably not the case, since unpublished measurements by Mrs. C. G. Le Fèvre have shown that benzil in benzene solution has strong ***negative*** electric double refraction (Kerr effect) whereas phenanthraquinone, on the other hand, produces a high *positive* effect. A *cis*-form of benzil would resemble phenanthraquinone in the disposition of its resultant moment along a direction of high polarisability and therefore also in the algebraical sign of its Kerr constant (large, positive); a *trans*-form, being non-polar, would have a small positive value. A mixture of the type under consideration, therefore, should show a *positive* effect.

We conclude that the third possibility probably occurs. The effective degree of departure ($\chi°$) from a coplanar arrangement of the two ketone groups can be easily calculated, since, from geometry, the resultant moment should be :

$$R = \mu \cos 30° \sqrt{2(1 + \cos \chi)}.$$

From this expression, together with the experimentally determined moments (see Tables on pp. 1615 and 1616), it appears that, in all the media the benzil molecules have closely similar configurations in which the two planes containing the  $\text{—}\underset{\underset{\displaystyle O}{\|}}{C}\text{—}\underset{\underset{\displaystyle O}{\|}}{C}\text{—}$ links are inclined at 90—100° to one another.*

If the present conclusions are correct, benzil becomes the third molecule for which a " skew " structure has been proposed, the other two being hydrogen peroxide and hydrazine (Penney and Sutherland, *loc. cit.*). These were considered to adopt this unusual configuration because the electron clouds on the oxygen or nitrogen atoms, respectively, do not possess axial symmetry about the O–O (or N–N) line and in consequence give rise to an interaction which, when allowance has been made for all other types of interaction, is found to be a dominant factor in setting the azimuthal angle at approximately the perpendicular value. It would seem that a similar reason ***mutatis mutandis*** might be stated for benzil, since the electron clouds on its two central carbon atoms will presumably lack symmetry roughly as much as the corresponding atoms of hydrogen peroxide and hydrazine. On such a view, diacetyl should possess a configuration of this type also, since for both it

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* It is noteworthy that Lonsdale and Knaggs (*Nature*, 1939, **143**, 1023) have recently reported that a skew structure for the molecules in crystalline benzil is indicated by an analysis now in progress based on complete *X*-ray measurements and a new determination of the magnetic anisotropy. Five other obvious configurations are already eliminated.

and benzil the central carbon pair have the same immediate electronic environment. For the investigation of this point we have examined the dielectric polarisation of diacetyl in benzene, finding ${}_{\mathrm{T}}P_{\infty} = 90{\cdot}5$ c.c. at 25°, whence $\mu = 1{\cdot}8_4$. This result has an additional interest, since, by comparison with the measurements recorded by Zahn (*Physical Rev.*, 1932, **40**, 291), the effects which changes of state and temperature might have on the configuration are indicated. Zahn reports the total polarisation of diacetyl vapour between 66° and 231°, at which limits the values are 51·90 and 49·66 c.c., corresponding to apparent moments of 1·25 and 1·48 respectively. From these figures estimates of the azimuthal angles, $\chi°$, can be made by the method used above for benzil. Some uncertainty must exist concerning the magnitude of the components acting along the directions of the C=O links, but their most likely value is that of the moment of acetone, *viz.*, 2·85 (Zahn, *Physikal. Z.*, 1932, **33**, 686). The results are tabulated below, and to show the effect of a variation of the components, χ has been calculated also for $\mu = 2{\cdot}5$ and 3·0.

Azimuthal Angle for Diacetyl.

Temp. …………	25°			55·8°			231·3°		
State …………	Solution in benzene.			Vapour.			Vapour.		
Moment, D. ……	1·84			1·25			1·48		
Component ……	2·5	2·85	3·0	2·5	2·85	3·0	2·5	2·85	3·0
$\chi°$ ………………	130°	136°	138°	146½°	150½°	152°	140°	145°	147°

It is seen that the configuration, although apparently not very sensitive to temperature changes (a range of *ca.* 170° altering χ by approximately 5° only), and affected by the presence of the solvent (in this respect recalling the ethylene dihalides), is clearly much more *trans-* than is that of benzil. Among the factors determining the structure of the latter molecule, therefore, there must be some which are additional to those which are sufficient alone for the cases of hydrogen peroxide, etc.

The causes likely to be most operative in diacetyl, benzil, and such molecules are: (1) electrostatic attractions and repulsions between the highly polar ketonic groups, (2) attractions arising from "dispersion" forces (van der Waals attractions) particularly between the phenyl groups, and (3) repulsions ("steric hindrances") between the nearer carbon and hydrogen atoms of the phenyl groups and the oxygen atoms; these must be so strong for the more completely *cis*-configurations, in which certain interatomic distances would obviously be required to approach the values proper for covalent union, that such configurations should be impossible. Since the polarities of the C=O links in diacetyl and benzil are roughly the same, it is obvious that the cause of the difference in configuration between these two molecules must be sought in effects such as (2) and (3) rather than (1).

The electrostatic effect (1) can be estimated *a priori*; effects (2) and (3) are much less accessible. To examine the present suggestion, therefore, the electrostatic energies associated with different configurations have been calculated on a basis of the following assumptions: that the carbon valency angles are 120° throughout; the C–C distances, 1·54 A.; the C=O distances 1·38 A.; and that two components of magnitude $3{\cdot}2_3$ are acting along the C–O directions and are situated at points midway between the centres of these atoms. Then, if d_1 and d_2 are certain dimensions in the completely *cis*-form (see Fig. 3), the separation of the points of action of the components during intramolecular rotation is given by $d = \sqrt{d_1^2 + 4d_2^2 \sin^2 (\chi/2)}$, so that, since the reciprocal energy of two dipoles is given by $E = (\mu^2/d^3)(\cos\chi - 3\cos\alpha_1\cos\alpha_2)$ and $\alpha_1 = \alpha_2 = 120°$ in the present case, we have

$$E = 10{\cdot}43\left[\frac{(\cos\chi - 0{\cdot}75)}{(4{\cdot}97 + 1{\cdot}426\sin^2\{\chi/2\})^{3/2}}\right] \times 10^{-12}\ \text{ergs/mol.}$$

Evaluation gives the following data (curve *A*, Fig. 4):

$\chi =$	0°	30°	60°	90°	120°	150°	180°	
$E =$	0·24	0·11	−0·22	−0·58	−0·88	−1·07	−1·13	$\times 10^{-12}$ ergs/mol.

which show the completely *trans*-form to be the most stable.

The dispersion forces (effect 2) will be largest for small values of χ and will fall off rapidly as this angle increases. An attempt has been made to estimate their magnitudes by using Slater and Kirkwood's formula (*Physical Rev.*, 1931, **37**, 682) for the reciprocal binding energy between two atoms, *viz.*, $-E = 11{\cdot}25 \times 10^{-24} n^{1/2} \alpha^{3/2} R^{-6}$ ergs/mol., in which n is the number of electrons in the outermost shell of the atom under consideration and α is the polarisability. For the present application we consider 48 electrons grouped at the centres of the benzene rings whose polarisabilities are $1{\cdot}03 \times 10^{-28}$ c.c. The distances between these centres, during rotation, are found as before from $(d_3^2 + 4d_4^2 \sin^2 \chi/2)^{1/2}$ (cf. Fig. 3). The following results emerge :

$\chi =$	0°	20°	45°	90°	135°	180°	
$E =$	−0·32	−0·29	−0·19	−0·07	$-0{\cdot}03_5$	$-0{\cdot}02_7$	$\times 10^{-12}$ ergs/mol.

They are plotted as curve *B* (Fig. 4). This, when superimposed on curve *A*, still indicates that the *trans*- is the most stable configuration.

Evidently the third factor—steric repulsion—is not negligible. This seems likely since, in crystals and liquids, molecules do not approach nearer than 3—4 A., and therefore between the parts of a flexible molecule interatomic separations less than this must be accompanied by an increase of configurational potential energy. Thus the completely *cis*-, flat form of benzil, in which the *o*-carbon atoms would make a mutual approach of *ca.* 1·5 A., is much less likely than one in which the repulsion is avoided by a turning of the aromatic rings into a face-to-face orientation. However, even in the latter case in the course of a complete revolution of the benzoyl groups, points will be reached when the number 1 C atoms of each phenyl group are at a critical separation, beneath which steric repulsion must set in; in the same way there will be points for the two oxygen atoms, both mutually and with regard to the above carbon atoms. Estimates of these critical separations can be reasonably made by using Stuart's " Wirkungsradien " (*Z. physikal. Chem.*, 1935, *B*, **27**, 350), from which it would appear that two uncombined carbon atoms never freely approach nearer than 3·34 A., two oxygen atoms similarly never nearer than 2·72 A., and a carbon and an oxygen atom never nearer than 3·03 A. The values of χ corresponding to these distances are easily calculated (see above). At a value of $\chi = 0°$, the two oxygen atoms have not reached their minimum separation, but the carbon atoms reach theirs at 82°, and the carbon–oxygen pair theirs at 142°. These calculations therefore suggest that only configurations with χ roughly between 80° and 140° are likely to be permitted by steric forces. Fig. 4 summarises this discussion graphically. Curve *B* should accurately have been derived by summing the mutual energies of each of the centres (carbon and hydrogen atoms) of one phenyl group in relation to all the centres of the other phenyl group. It is clear that the sum of the sixth powers of these interatomic separations is *less* than the sixth power of the distances between the centres of the phenyl groups, *i.e.*, the distances actually used in drawing *B*. This curve, therefore, should reach a lower negative value for $\chi = 0°$ than is

FIG. 3.

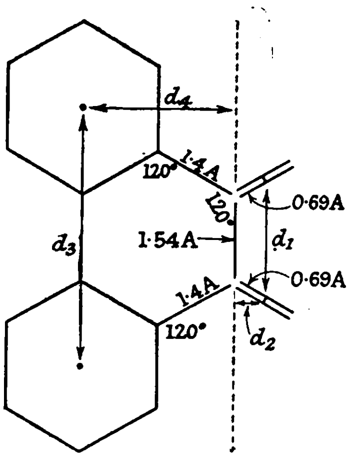
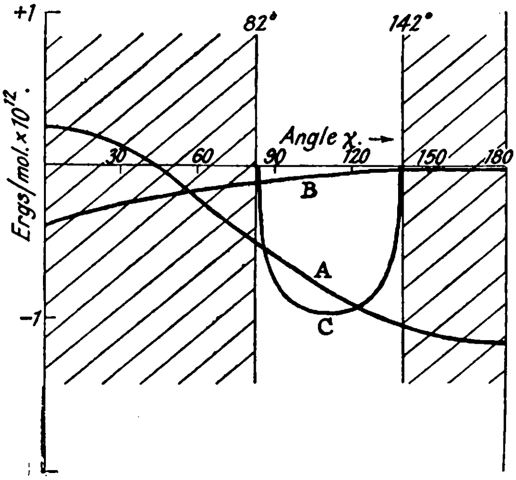


FIG. 4.



depicted. In these circumstances it is not unreasonable to suppose that the potential energy of the benzil molecule assumes a form such as curve *C*, with a minimum at *ca.* 100°, in conformity with our present results.

Finally, if the differences between the configurations of diacetyl and benzil are attributed to the smaller dispersion forces operating in the former molecule, the minimum of the resultant curve will shift towards larger values of χ. This is again in agreement with the experimental data.

EXPERIMENTAL.

Materials.—Commercial benzil and phenanthraquinone were recrystallised from alcohol; m. p.'s 95° and 205° (after drying at 100°). The acenaphthaquinone was prepared from acenaphthene by oxidation with acetic acid and sodium dichromate (Graebe and Gfeller, *Annalen*, 1893, **276**, 4; *Ber.*, 1887, **20**, 659; *ibid.*, 1892, **25**, 654). (We are indebted to Mr. C. C. Evans for assistance with this operation.) After sublimation and several crystallisations from benzene, it had m. p. 245°.

The solvents were of A.R. grade, further purified by drying with metallic sodium in all cases, except chloroform (for which calcium chloride was used) and carbon tetrachloride (for which sodium sulphate was used), decantation, and fractionation. The benzene was then partly frozen, and the solid, when remelted, stored over sodium. The carbon disulphide was treated with solid potassium permanganate, dried over anhydrous sodium sulphate, distilled, and kept over calcium chloride.

Measurements.—These were made by using the apparatus and method described in "Dipole Moments" (Methuen, 1938, pp. 29—35). Observations are recorded below under the headings: w_1, the weight fractions of the solutes in the solutions; ε, the dielectric constant at *ca.* 1200 kc.; *d*, the density; *n*, the refractive index for sodium light (compared with the *d* and *n* values respectively of benzene at 25° shown in the tables). The specific polarisations and refractions of the solutions are shown under p_{12} and r_{12}. From these data the factors $\alpha\varepsilon_2$ and βd_2 (subscripts 1 and 2 refer to the solute and the solvent respectively) have been obtained as averages from

$$\alpha\varepsilon_2 = \Sigma(\varepsilon_{12} - \varepsilon_2)/\Sigma w_1 \text{ and } \beta d_2 = \Sigma(d_{12} - d_2)/\Sigma w_1$$

The total molecular polarisations at infinite dilution are then given by

$$_{\mathrm{T}}P_\infty = M[p_2(1 - \beta) + C\alpha\varepsilon_2]$$

where *M* is the molecular weight of the solute, p_2 the specific polarisation of the solvent, and *C* a constant for the latter: $C = 3/d_2(\varepsilon_2 + 2)^2$ (cf. Le Fèvre and Vine, J., 1937, 1805). To enable comparisons to be made between these results and those obtained by graphical extrapolation, P_1 for each solution, evaluated in the usual way [from $p_1 = p_2 + (p_{12} - p_2)/w_1$], is also shown.

The dielectric-constant measurements recorded below in the cases of *n*-hexane, dioxan, carbon tetrachloride, and carbon disulphide were relative to benzene, for which the standard figure of 2·2725 at 25° was taken (Hartshorn and Oliver, *Proc. Roy. Soc.*, 1929, *A*, **123**, 664). For chloroform Ball's value for the dielectric constant (J., 1930, 570) was used.

Benzil in benzene.

$100w_1$.	ε_{25°.	$d_{4^\circ}^{25^\circ}$.	p_{12}.	P_1.	n_{D}.	r_{12}.	$[R_L]_{\mathrm{D}}$.
0	2·2725	0·87378	0·34086	—	1·49724	0·33503	—
0·9571	2·3435	0·87593	0·35312	340·6	1·49815	0·33472	63·6
1·6696	2·3966	0·87746	0·36202	337·7	1·49869	0·33445	63·1
2·6663	2·4734	0·87982	0·37436	335·4	1·49957	0·33405	62·6
3·3546	2·5297	0·88141	0·38314	336·3	1·50029	0·33385	63·0
3·6801	2·5515	0·88214	0·38647	331·9	1·50048	0·33368	62·7
4·9738	2·6553	0·88513	0·40172	328·5	1·50164	0·33321	62·5
6·3544	2·7689	0·88829	0·41757	325·1	1·50282	0·33269	62·6

$\alpha\varepsilon_2 = 7{\cdot}66$; $p_\infty = 1{\cdot}6930$; mean $[R_L]_{\mathrm{D}} = 63$ c.c.*; $\beta = 0{\cdot}260$; $_{\mathrm{T}}P_\infty = 355{\cdot}5$ c.c.; $C = 0{\cdot}18809$; $\mu = 3{\cdot}76$.

Phenanthraquinone in benzene.

0·05302	2·2818	0·87392	0·34255	733·9	1·49730	0·33501	61·8
0·10523	2·2899	0·87410	0·34399	689·7	1·49738	0·33499	61·8
0·20951	2·3082	0·87443	0·34726	706·3	1·49756	0·33496	(62·7)
0·26860	2·3183	0·87460	0·34905	705·1	1·49761	0·33493	61·9

$\alpha\varepsilon_2 = 16{\cdot}81_5$; $p_\infty = 3{\cdot}3862_5$; mean $[R_L]_{\mathrm{D}} = 62$ c.c.; $\beta = 0{\cdot}347$; $_{\mathrm{T}}P_\infty = 704{\cdot}3$ c.c.; $\mu = 5{\cdot}57$.

* Two measurements of the refractivity of benzil in benzene solution are recorded by Anderlini (*Gazzetta*, 1895, **25**, 127); from their mean, $[R_L]_\alpha$ is calculable as 63·5 c.c., in satisfactory agreement with the above results.

Benzil in benzene at 50°.

$100w_1$.	ϵ.	d.	p_{12}.	P_1.	$100w_1$.	ϵ.	d.	p_{12}.	P_1.
0	2·2232	0·84714	0·34190	—	2·9647	2·4149	0·85410	0·37523	307·9
1·1806	2·2979	0·84996	0·35529	310·0	4·1302	2·4896	0·85686	0·38721	302·2
2·1385	2·3615	0·85219	0·36631	311·5					

$\alpha\epsilon_2 = 6{\cdot}450$; $p_\infty = 1{\cdot}5275$; $\beta = 0{\cdot}278_2$; ${}_{\mathrm{T}}P_\infty = 320{\cdot}8$ c.c.; $C = 0{\cdot}19856$; $\mu = 3{\cdot}6_8$.

Higashi (*Bull. Chem. Soc. Japan*, 1938, **13**, 158) has recorded measurements relating to benzil in carbon tetrachloride and benzene solutions at 25° and 50°, from which it appears that such a temperature interval is without effect upon the moment of the solute. The above observations were made to check this point; those which follow were obtained in redistilled sodium-dried decalin, b. p. 192°, with which higher temperatures could be more conveniently reached. The temperature–dielectric constant relation for the solvent is derived from the results given in *Trans. Faraday Soc.*, 1938, **34**, 1127.

Benzil in decalin.

$100w_1$.	ϵ_{t°.	$d_{4^\circ}^{t^\circ}$.	p_{12}.	P_1.	$100w_1$.	ϵ_{t°.	$d_{4^\circ}^{t^\circ}$.	p_{12}.	P_1.
Temperature 25°.					Temperature 50°.				
0	2·099	0·87897	0·30530	—	0	2·062	0·86096	0·30367	—
0·9918	2·157	0·88190	0·31560	287·9	0·9918	2·112	0·86293	0·31338	269·4
1·3139	2·174	0·88237	0·31876	283·5	1·3139	2·127	0·86332	0·31631	265·8
1·6715	2·197	0·88308	0·32296	289·3	1·6715	2·146	0·86412	0·31987	267·3

$\alpha\epsilon_2 = 5{\cdot}80_8$; $p_\infty = 1{\cdot}3938$ c.c.; $\beta = 0{\cdot}298_6$; ${}_{\mathrm{T}}P_\infty = 292{\cdot}7$ c.c.; $C = 0{\cdot}20314$; $\mu = 3{\cdot}33$.

$\alpha\epsilon_2 = 5{\cdot}00_4$; $p_\infty = 1{\cdot}2940$ c.c.; $\beta = 0{\cdot}2187$; ${}_{\mathrm{T}}P_\infty = 271{\cdot}7$ c.c.; $C = 0{\cdot}21118$; $\mu = 3{\cdot}31$.

Temperature 70°.					Temperature 90°.				
0	2·034	0·84682	0·30269	—	0	2·008	0·83046	0·30284	—
0·9918	2·080	0·84887	0·31183	257·1	0·9918	2·051	0·83249	0·31165	250·1
1·3139	2·098	0·84927	0·31549	268·1	1·3139	2·064	0·83283	0·31436	247·7
1·6715	2·113	0·85005	0·31834	260·2	1·6715	2·081	0·83360	0·31776	251·1

$\alpha\epsilon_2 = 4{\cdot}75_2$; $p_\infty = 1{\cdot}2677$ c.c.; $\beta = 0{\cdot}2295$; ${}_{\mathrm{T}}P_\infty = 266{\cdot}2$ c.c.; $C = 0{\cdot}21770$; $\mu = 3{\cdot}34$.

$\alpha\epsilon_2 = 4{\cdot}32_5$; $p_\infty = 1{\cdot}2063$ c.c.; $\beta = 0{\cdot}228$; ${}_{\mathrm{T}}P_\infty = 253{\cdot}3$ c.c.; $C = 0{\cdot}22488$; $\mu = 3{\cdot}3_4$.

Benzil in n-*hexane.* *Benzil in dioxan.*

$100w_1$.	ϵ_{25°.	$d_{4^\circ}^{25^\circ}$.	p_{12}.	P_1.	$100w_1$.	ϵ_{25°.	$d_{4^\circ}^{25^\circ}$.	p_{12}.	P_1.
0	1·8876	0·66669	0·34246	—	0	2·2093	1·02920	0·27914	—
0·34077	1·9027	0·66763	0·34645	317·8	1·6025	2·3495	1·03108	0·30091	343·9
0·58885	1·9133	0·66838	0·34918	311·6	3·7272	2·5418	1·03352	0·32846	337·6
0·70655	1·9186	0·66874	0·35054	312·1					
0·76155	1·9208	0·66888	0·35111	310·4					
0·86665	1·9255	0·66918	0·35232	310·8					

$\alpha\epsilon_2 = 4{\cdot}38$; $p_\infty = 1{\cdot}4993$ c.c.; $\beta = 0{\cdot}430$; ${}_{\mathrm{T}}P_\infty = 314{\cdot}9$ c.c.; $C = 0{\cdot}29774$; $\mu = 3{\cdot}49$.

$\alpha\epsilon_2 = 8{\cdot}87$; $p_\infty = 1{\cdot}7068$ c.c.; $\beta = 0{\cdot}113$; ${}_{\mathrm{T}}P_\infty = 358{\cdot}4$ c.c.; $C = 0{\cdot}16451$; $\mu = 3{\cdot}78$.

Phenanthraquinone in dioxan.

0·47171	2·3029	1·03044	0·29385	706·7	0·77396	2·3633	1·03124	0·30298	698·8

$\alpha\epsilon_2 = 19{\cdot}88$; $p_\infty = 3{\cdot}4781$ c.c.; $\beta = 0{\cdot}256$; ${}_{\mathrm{T}}P_\infty = 723{\cdot}5$ c.c.; $\mu = 5{\cdot}66$.

Benzil in carbon tetrachloride. *Benzil in carbon disulphide.*

0	2·2270	1·58549	0·18308	—	0	2·6402	1·25814	0·28095	—
0·7037	2·3135	1·58172	0·19258	322·0	0·6503	2·7059	1·25765	0·28824	294·4
1·3507	2·3945	1·57822	0·20107	318·1	1·2055	2·7635	1·25687	0·29455	296·0
2·0489	2·4847	1·57447	0·21027	317·1	1·9012	2·8374	1·25594	0·30243	296·3
2·7894	2·5799	1·57034	0·21967	313·9	2·6621	2·9184	1·25495	0·31081	298·2
3·4388	2·6620	1·56689	0·22752	209·8	3·5751	3·0189	1·25368	0·32086	293·4

$\alpha\epsilon_2 = 12{\cdot}58$; $p_\infty = 1{\cdot}5777$ c.c.; $\beta = 0{\cdot}341$; ${}_{\mathrm{T}}P_\infty = 331{\cdot}3$ c.c.; $C = 0{\cdot}10590$; $\mu = 3{\cdot}60$.

$\alpha\epsilon_2 = 10{\cdot}44$; $p_\infty = 1{\cdot}4630$ c.c.; $\beta = -0{\cdot}0923$; ${}_{\mathrm{T}}P_\infty = 307{\cdot}2$ c.c.; $C = 0{\cdot}11074$; $\mu = 3{\cdot}44$.

Phenanthraquinone in carbon disulphide.

0·040805	2·6514	1·25815	0·28219	690·5	0·061428	2·6569	1·25816	0·28279	681·5

$\alpha\epsilon_2 = 27{\cdot}29$; $p_\infty = 3{\cdot}2965$ c.c.; $\beta = 0{\cdot}0233$; ${}_{\mathrm{T}}P_\infty = 685{\cdot}7$ c.c.; $\mu = 5{\cdot}50$.

Benzil in chloroform.

$100w_1$.	$\epsilon_{25°}$.	$d_{4°}^{25°}$.	p_{12}.	P_1.
0	4·724	1·47910	0·37444	—
0·6461	4·843	1·47683	0·38027	268·1
1·3432	4·975	1·47432	0·38655	268·0
1·4531	4·992	1·47395	0·38735	265·6
2·0780	5·115	1·47181	0·39295	265·7
2·8148	5·258	1·46910	0·39933	264·3

$a\epsilon_2$ = 18·75; p_∞ = 1·3051 c.c.; β = −0·239;
${}_{\mathrm{T}}P_\infty$ = 274·1 c.c.; C = 0·044861; μ = 3·21.

Phenanthraquinone in chloroform.

$100w_1$.	$\epsilon_{25°}$.	$d_{4°}^{25°}$.	p_{12}.	P_1.
$0{\cdot}1437_3$	4·790	1·47897	0·37741	507·7
$0{\cdot}2971_5$	4·865	1·47882	0·38071	516·8
$0{\cdot}8069_4$	5·112	1·47830	0·39111	507·6

$a\epsilon_2$ = 46·89; p_∞ = 2·5025 c.c.; β = −0·0656;
${}_{\mathrm{T}}P_\infty$ = 520·5 c.c.; μ = 4·71.

Acenaphthaquinone in benzene.

0	2·2725	0·87378	0·34086	—
0·037967	2·2809	0·87397	0·34236	781·1
0·075298	2·2894	0·87405	0·34392	801·7
0·100904	2·2963	0·87416	0·34516	837·6

$a\epsilon_2$ = 22·93; p_∞ = 4·5007 c.c.;
$[R_L]_{\mathrm{D}}$ = 55 c.c.*; β = $0{\cdot}392_2$;
${}_{\mathrm{T}}P_\infty$ = 819·1 c.c.; C = 0·18809; μ = 6·08.

Diacetyl in benzene.

1·0125	2·3118	0·87430	0·34797	89·7
2·0228	2·3507	0·87481	0·35488	88·9
2·6442	2·3754	0·87515	0·35919	88·9
3·7237	2·4176	0·87571	0·36644	88·4

$a\epsilon_2$ = $3{\cdot}88_7$; p_∞ = 1·0519 c.c.;
$[R_L]_{\mathrm{D}}$ = 20·9 c.c.†; β = $0{\cdot}590_3$;
${}_{\mathrm{T}}P_\infty$ = 90·5; μ = 1·84.

* Calc. from : naphthalene = 44·4, benzil = 63, benzene = 26·2, hydrogen = 1·1 c.c.

† Calc. from : $n_{\mathrm{D}}^{18{\cdot}5°}$ = 1·39331, $d_{4°}^{18{\cdot}5°}$ = 0·9808 (Brühl, *J. pr. Chem.*, 1894, **50**, 140).

Previous Measurements.—Dielectric-polarisation data for benzil are contained in papers by Hassel and Naeshagen (*Z. physikal. Chem.*, 1929, *B*, **6**, 152), Weissberger and Sängewald (*Physikal. Z.*, 1929, **30**, 268), and Higashi (*loc. cit.*). Their solvents, temperatures, and results are given below :

Author(s).	Solvent.	Temp.	${}_{\mathrm{T}}P_\infty$, c.c.	μ.	Author(s).	Solvent.	Temp.	${}_{\mathrm{T}}P_\infty$, c.c.	μ.
H. and N.	C_6H_6	18°	292·5 *	3·7	Higashi	C_6H_6	50°	313	$3{\cdot}6_2$
W. and S.	C_6H_6	25	not quoted	3·2	,,	CCl_4	25	318	$3{\cdot}5_2$
Higashi	C_6H_6	25	333	$3{\cdot}6_2$	,,	CCl_4	50	291	$3{\cdot}4_6$

* ${}_\infty P_{\mathrm{A}+\mathrm{O}}$.

As various methods of allowing for atomic polarisation were employed in calculating the final moments here listed, comparison with the present data is best made with the total polarisation figures. When this is done, our results are seen to agree very satisfactorily with those of Hassel and Naeshagen and to be slightly higher than those of Higashi.

St.-Antoine (*Compt. rend.*, 1928, **186**, 1429) found the dielectric constant of molten benzil to fall from 13·04 at 95° to 12·12 at 120°. The last figure, combined with one of the density determinations recorded by Grinakowski (*Chem. Zentr.*, 1913, **84**, II, 2076), gives a total polarisation of only 154 c.c., corresponding to a moment of 2·4. According to Cauwood and Turner (J., 1915, **107**, 281), the dielectric constant just below the m. p. at 95° is 4·14, from which it is evident that, unless the solid is much heavier than the liquid, the polarisation still greatly exceeds the molecular refraction.

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