Dipole Moments of Benzil and Stilbene Dichloride.

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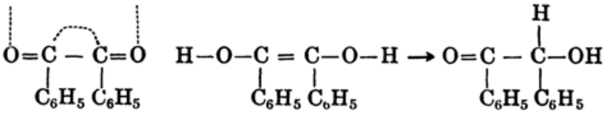
In a famous paper⁽¹⁾ published in 1899, J. Thiele pointed out that benzil might be regarded as having conjugated double bonds. On reduction, its double bonds were supposed to move to the centre, giving an unsaturated glycol, and to prove this view, he succeeded in obtaining the *cis*- and *trans*-forms of the enolic diacetate.



$$\underset{\text{Benzil.}}{O{=}\underset{C_6H_5}{C}-\underset{C_6H_5}{C}{=}O} \qquad \underset{\text{Enolic isomer.}}{H{-}O{-}\underset{C_6H_5}{C}=\underset{C_6H_5}{C}{-}O{-}H} \rightarrow \underset{\text{Benzoin.}}{O{=}\underset{C_6H_5}{C}-\overset{H}{\underset{C_6H_5}{C}}{-}OH}$$

Benzil. Enolic isomer. Benzoin.

Translating this into modern words, the case for benzil may be said as intimately related to single bond-double bond resonance. If the C–C

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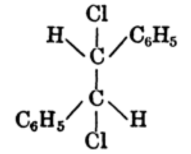
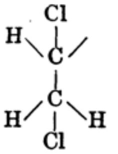
(1) Thiele, *Ann.*, **306** (1899), 87, 142. See also Waters, "Physical Aspects of Organic Chemistry," 373, London (1935).

single bond aquires a considerable amount of double bond character due to this quantum mechanical resonance, intramolecular rotation should be greatly hindered, and its direct consequence would appear in the temperature independence of dipole moment.(2)

Having this view in mind, the dipole moment of benzil was measured in benzene and carbon tetrachloride at 25 and 50°C. The reason for choosing two different solvents is to check the specific action of solvents.





The dipole moment of α-stilbene dichloride in benzene and carbon tetrachloride was also studied. This substance resembles $CH_2Cl{\cdot}CH_2Cl$ in structural formula, the only difference being the existence of two C_6H_5 groups instead of two H atoms. From the comparison with the moment of $CH_2Cl{\cdot}CH_2Cl$ in the corresponding solvent, the effect of introducing big phenyl groups was sought.

Preparation of Materials. *Benzil.* Benzoin was first prepared from benzaldehyde and HCN and then was oxidised to benzil. Material thus obtained was recrystallised from alcohol and then from benzene. M.p. 95°C. Benzil was also synthesised from stilbene dichloride, and the dielectric study on it was made for comparison's sake.

α-Stilbene dichloride. This material was obtained by the addition of chlorine to stilbene (purest) of Fränkel and Landau. Recrystallised from alcohol and then from the mixture of benzene and hexane. M.p. 191°C. At first the material recrystallised from alcohol and dried was examined; and the slightly higher moment of 1.50 D was obtained; this seems to be due to the remaining alcohol.

Benzene, hexane, and carbon tetrachloride. Materials from the Schering-Kahlbaum A. G. and the Nippon Zyunyaku Co. were treated as in earlier work.(3)

Experimental Results. As the apparatus and the method of measurement of the dielectric constant were described in a previous paper,(3)(4) only some improvements(5) which were made later will be reported here. In the oscillation circuit which contained the dielectric cell, a tetrode

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(2) Kozima and Mizushima, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **31** (1937), 296.

(3) Higasi, *ibid.*, **24** (1934), 57.

(4) Mizushima, Morino, and Higasi, *ibid.*, **25** (1934), 159.

(5) Cordial thanks are due to Mr. T. Sibata for his kindness in helping the writer in making these improvements.

bulb "Mazda" UY 236 with a screening grid and an indirectly heated cathode, were employed (Fig. 1.). For the switch which connects the dielectric cell to the oscillating circuit, a pen-form one (Fig. 2.) was used in the place of the former. A radio set of ordinary UY 24B, UY 47B, KX 12B type with a slight improvement was satisfactorily utilized for the purpose of amplifying the beat note.

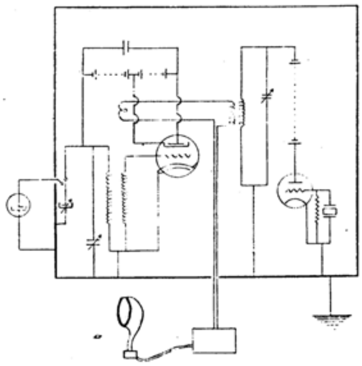

Fig. 1.

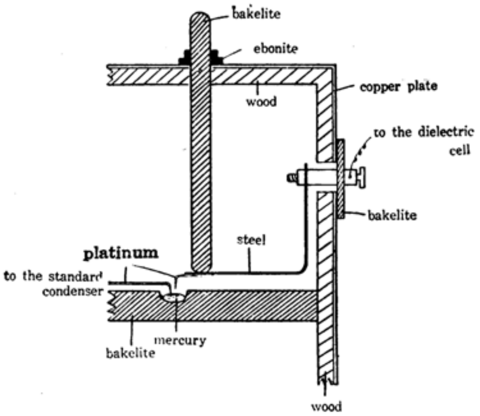

Fig. 2.

Symbols and formulæ used in this article are as follows:

ω : the concentration of the solute in the gram percentage.

ε, ε_1 : the dielectric constant of the solution and the solvent respectively.

d, d_1 : the density of the solution and the solvent respectively.

p_{12}, p_1 : the specific polarization of the solution and the solvent,

$$p_{12}=\frac{\varepsilon-1}{\varepsilon+2}\cdot\frac{1}{d} \quad \text{and} \quad p_1=\frac{\varepsilon_1-1}{\varepsilon_1+2}\cdot\frac{1}{d_1}, \quad \text{respectively.}$$

P_2 : the molar polarization

$$P_2=M_2\left(p_1+\frac{p_{12}-p_1}{\omega}\right),$$

where M_2 denotes the molecular weight of the solute.

μ : the dipole moment, which is calculated in this article as follows,

$$\mu=0.01273\left[P_{2\infty}-(P_E+P_A)\right]^{\frac{1}{2}}T^{\frac{1}{2}}\fallingdotseq 0.01273(P_{2\infty}-(1+\delta)MR_D)^{\frac{1}{2}}T^{\frac{1}{2}}$$

$$\delta=0.05\sim0.15\,.$$

The estimation of the atomic polarisation in the determination of the dipole moment has been quite arbitrary and sometimes confusing. In the present case where the temperature dependence in moment is to be examined, the total neglect of the atomic polarisation appears to be much more erratic. In this paper, the atomic polarisation was estimated as 5% of the molecular refraction, MR_D after Groves and Sugden⁽⁶⁾ (denoted by μ) and also as 15% after Wolf's school⁽⁷⁾ (denoted by μ'). As is clear by the results, the difference in the choice of the atomic polarization hardly affects the temperature dependence (See Table 2).

The results are shown in Table 1. The results on benzil from stilbene dichloride are also recorded in the same table. A glance at it will show that there is no difference in moment in benzene solution between this and the sample from benzaldehyde.

Discussion of Results. The dipole moment of benzil in benzene solution at 25°C. was found as 3.71 D by Hassel and Naeshagen⁽⁸⁾ and 3.2 D by Sängewald and Weissberger.⁽⁹⁾ The result of the present measurement, $\mu = 3.62$ D lies between them. The moment of α-stilbene dichloride

Table 1.
Benzil (prepared from benzoin).

In benzene at 25°C.

ω	ε	d	p_{12}	p_2	P_2
0.00	2.273	0.87336	0.34112	—	—
0.904	2.3379	0.87525	0.35238	1.587	333
1.610	2.3904	0.87684	0.36117	1.586	333
2.995	2.4951	0.87799	0.37883	1.599	336

$P_{2\infty} = 333$ c.c., $MR_D = 58.92$ c.c.,
$P_A = 5\%\ MR_D$, $P_E + P_A = 61.87$ c.c., $\mu = 3.62$D
$P_A = 15\%\ MR_D$, $P_E + P_A = 67.76$ c.c., $\mu' = 3.58$D

In benzene at 50°C.

0.00	2.225	0.84607	0.34269	—	—
0.904	2.2826	0.84824	0.35307	1.491	313
1.610	2.3281	0.84987	0.36106	1.484	312
2.995	2.4176	0.85342	0.37601	1.455	306

$P_{2\infty} = 313$ c.c., $P_E + P_A = 61.87$ c.c., $\mu = 3.62$D
$P_E + P_A = 67.76$ c.c., $\mu' = 3.58$D

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(6) Groves and Sugden, *J. Chem. Soc.*, **1935**, 971.
(7) Wolf and Trieschmann, *Z. physik. Chem.*, B, **14** (1931), 346.
(8) Hassel and Naeshagen, *ibid.*, B, **6** (1929), 152.
(9) Sängewald and Weissberger, *Physik. Z.*, **30** (1929), 268.

In carbon tetrachloride at 25°C.

ω	ε	d	p_{12}	p_2	P_2
0.00	2.232	1.58434	0.18374	—	—
0.6403	2.3094	1.58044	0.19225	1.512	318
0.910	2.3430	1.57888	0.19586	1.516	319
2.096	2.4912	1.57260	0.21114	1.491	314

$P_{2\infty} = 318$ c.c., $P_E+P_A = 61.87$ c.c., $\mu = 3.52$D
$P_E+P_A = 67.76$ c.c., $\mu' = 3.48$D

In carbon tetrachloride at 50°C.

0.00	2.183	1.53501	0.18424	—	—
0.6403	2.2497	1.53217	0.19193	1.385	291
0.910	2.2787	1.53097	0.19520	1.389	292
2.096	2.4104	1.52465	0.20974	1.400	294

$P_{2\infty} = 291$ c.c., $P_E+P_A = 61.87$ c.c., $\mu = 3.46$D
$P_E+P_A = 67.76$ c.c., $\mu' = 3.42$D

Benzil (prepared from stilbene dichloride)

In benzene at 25°C.

0.00	2.273	0.87353	0.34105	—	—
1.150	2.3569	0.87604	0.35551	1.599	336
1.491	2.3817	0.87708	0.35953	1.581	332

$P_{2\infty} = 334$ c.c., $P_E+P_A = 61.87$ c.c., $\mu = 3.63$D
$P_E+P_A = 67.76$ c.c., $\mu' = 3.59$D

In hexane at 25°C.

0.00	1.8871	0.66547	0.34293	—	—
0.524	1.9103	0.66729	0.34886	1.473	309
0.720	1.9182	0.66763	0.35100	1.463	307
1.442	1.9500	0.66966	0.35915	1.467	308

$P_{2\infty} = 308$ c.c., $P_E+P_A = 61.87$ c.c., $\mu = 3.45$D
$P_E+P_A = 67.76$ c.c., $\mu' = 3.41$D

α-Stilbene dichloride.

In benzene at 25°C.

ω	ε	d	p_{12}	p_2	P_2
0.00	2.273	0.87353	0.34105	—	—
0.767	2.2819	0.87548	0.34195	0.4584	115.1
1.254	2.2872	0.87658	0.34252	0.4583	115.1

$P_{2\infty} = 115.1$ c.c., $MR_D = 68.63$ c.c.
$P_A = 5\%\ MR_D = 3.4$ c.c., $P_E + P_A = 72.0$ c.c., $\mu = 1.45$D

In carbon tetrachloride at 25°C.

0.00	2.225	1.58411	0.18303	—	—
0.1925	2.2286	1.58340	0.18349	0.422	105.8
0.1928	2.2289	1.58339	0.18352	0.437	109.6

$P_{2\infty} = 108$ c.c., $P_E + P_A = 72.0$ c.c., $\mu = 1.32$D

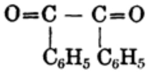
given by Weissberger and Sängewald⁽¹⁰⁾ is recorded as 1.27 D in benzene at 25°C. in contrast to 1.45 D of the present author. The difference between them seems rather large, but on account of the small solubility of this substance in benzene, high accuracy cannot be claimed in an earlier work—in the present case, the accuracy being $\mu = 1.45 \pm 0.06$ D.

The result of the present work on benzil is summarised in Table 2. The values of benzene solution are quite independent of temperature, while those in carbon tetrachloride solution slightly decrease with rising temperature.

Table 2. Dipole moment of benzil.

Solvent	C_6H_6		CCl_4	
t°C.	μ	μ'	μ	μ'
25	3.62	3.58	3.52	3.48
50	3.62	3.58	3.46	3.42

One must emphasize that this fact is incomprehensible by the ordinary chemical formula of benzil. If the carbon-carbon bond be purely single, from the analogy of $CH_2Cl{\cdot}CH_2Cl$,⁽⁴⁾ it is clear that the stable internal position should correspond to the *trans*-position and measurable increase in moment with rising temperature should result. And if we can attribute the constancy in moment in the benzene solution to the abnormal action



$$\underset{C_6H_5}{O{=}C} - \underset{C_6H_5}{C{=}O}$$

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(10) Weissberger and Sängewald, *Z. physik. Chem.*, B, **9** (1930), 133.

of the solvent, how can we explain the result obtained in carbon tetrachloride?

On the other hand, Hassel estimated the moment as 3.78 D, when free rotation occurs, and seemed to consider the agreement with the experimental value to be something more than mere coincidence. But free rotation, which is greatly hindered even in the case of $CH_2Cl\cdot CH_2Cl$ (with weaker mutual effect between the rotating groups), is very unlikely to occur.

From the result of Table 2, we may conclude as the following:

(1) The oscillatory rotation of the polar groups near the *trans*-position like that of $CH_2Cl\cdot CH_2Cl$ does not occur.

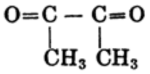
(2) The free rotation of the groups is improbable.

(3) Therefore, the carbon-carbon bond in benzil is different from the pure single bond.

As stated in the introduction, on account of the quantum mechanical resonance the carbon-carbon bond may acquire the double bond character. And the electronic structure of this bond has no longer the axial symmetry and tends to lock the groups either at the *cis*- or the *trans*-position. The dipole moment will be zero at the *trans*-position, while it will be very large at the *cis*-position.

The simplest explanation of the present experiment is to consider the existence of the *cis*-form only, (the *trans*-form having a much larger energy). From this assumption the constancy in the moment follows at once. Then we have to consider that the bond moments of this molecule become very different from the ordinary ones on account of the quantum mechanical resonance.

If, however, we consider the coexistence of the *trans*- and *cis*-configurations, the variation of the moment with temperature should result. And the observable value of the moment should be governed by the Maxwell-Boltzmann's law of distribution. The small decrease in the moment in CCl_4 solution might indicate this effect, but the temperature range of the present research is too small to draw a definite conclusion from it.



$$\begin{array}{cc} O{=}C - & C{=}O \\ | \quad & | \\ CH_3 & CH_3 \end{array}$$

It is very interesting to note that diacetyl is reported to behave just like ethylene dichloride. According to Zahn,(11) its moment increases from 1.25 D at 66° to 1.48 D at 231°. Therefore in spite of its similar structure to benzil, its carbon-carbon bond does not show any marked deviation from the single bond. Although further studies are desirable

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(11) Zahn, *Phys. Rev.*, ii, **40** (1932), 291.

to explain it, we should like to point out here that a similar behaviour in dipole moment was recently discovered by Mizushima and Kubo.(12)

Next, we will discuss the moment of α-stilbene dichloride.

Stilbene dichloride has two modifications (I and II of Fig. 3), and α-modification is supposed to be form I.

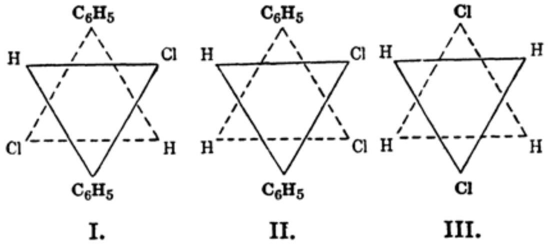

Fig. 3.

In Table 3 the comparison is made of the moments of this substance with those of ethylene dichloride in corresponding solvents.

As benzene is known to exert specific solvent action on ethylene dihalides, the results in carbon tetrachloride are first considered. It is remarkable that α-stilbene dichloride has almost the same moment as ethylene dichloride. As the moment of the rotating group $-CH(C_6H_5)Cl$ is supposed not to be much different from that of $-CH_2Cl$ (the moment of $C_6H_5CH_2Cl$ is 1.85 D in C_6H_6, while that of CH_3Cl is 1.86 D in vapour), this indicates that large phenyl groups do not exert a marked influence on the intramolecular rotation. This is easily understood by the consideration that in form I, the most stable position is the *trans*-position as regards to both phenyl groups and chlorine atoms, and the mutual effect of phenyl groups is not significant owing to large separation.

Table 3. Dipole moment at 25°C.

Solvent / Solute	CCl_4	C_6H_6
$C_6H_5CHCl\cdot C_6H_5CHCl$	1.32	1.45
$CH_2Cl\cdot CH_2Cl$	1.36(4)	1.75(4)

The moment in benzene is larger than that in carbon tetrachloride. But this tendency is not so strong as it is observed in ethylene dichloride. As an explanation of anomalous behaviour of this substance in benzene, the formation of a loose-complex was proposed in which the mutual posi-

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(12) Mizushima and Kubo, this Bulletin, **13** (1938), 174.

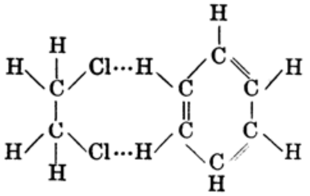

Fig. 4.

tion of two chlorine atoms tends to approach the *cis*-position[4] (Fig. 4.). According to this view, we might consider the case of α-stilbene dichloride as follows. This loose complex exists in the benzene solution of stilbene dichloride, too, giving a higher moment. But the two chlorine atoms cannot approach so near as in the case of ethylene dichloride because of the greater repulsion due to two phenyl groups.

Summary.

(1) The dipole moment of benzil was studied in three solvents and its temperature dependence was examined.

(2) The carbon-carbon bond of benzil is not a pure single bond and is probably a hybrid of single and double bonds. This is the result expected from Thiele's old idea of conjugated system and also from the quantum mechanical resonance.

(3) The dipole moment of α-stilbene dichloride was also studied in benzene and carbon tetrachloride solution. The result was compared with that of ethylene dichloride.

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