402. *The Dipole Moments of* cyclo*Hexa*-1 : 4-*dione*, cyclo*Pentadiene-benzoquinone, Benzoquinone, Carbon Suboxide, and Carbonyl Chloride.*

By (Mrs.) C. G. Le Fèvre and R. J. W. Le Fèvre.

The dielectric constants, densities, and refractive indexes of solutions of the above substances in either benzene or carbon tetrachloride at a known temperature have been measured by methods described in previous papers, and thence the total polarisations, molecular refractivities, orientation polarisations, and dipole moments of the solutes have been calculated in the usual way.

(a) *Dipole Moment of* cyclo*Hexa*-1 : 4-*dione*.—Our measurements indicate an apparent value of the dipole moment of 1·3 D, whereas, by the same method Hassel and Naeshagen (*Tids. Kjemi Berg.*, 1930, No. 7) had found 1·6 D. If, in our determination, 10% of $[R_L]_D$ is allowed for the atomic polarisation, a still lower value, *viz.*, 1·21 D, is obtained.

The equilibrium cis $\rightleftharpoons$ trans. From these results it should be possible to form an estimate of the proportions of the strainless forms present under the conditions of measurement. It is first necessary to establish the dipole moment of each of these forms, and these are calculated as follows : Let the two remaining valency directions of each of the ketonic carbon atoms be taken as meeting at 120° (Becker and Thorpe, J., 1920, **117**, 1579),* and let the usual radii, valency angles, etc., be adopted for the other carbon atoms in the molecule. A construction shows that in the *cis*-form the axes of the ketonic groups lie at an angle of about 133° to the horizontal plane containing the four methylene groups, and calculation on this basis indicates that, if the dipole moment of the keto-group be taken as 2·79 (*i.e.*, as in hexamethylacetone), the *cis*-configuration should exhibit a resultant moment of 4·1. For the *trans*-arrangement, in which the ketonic groups are in antiparallel alinement, the resultant moment is obviously nil.

At once, it can be seen that if the equilibrium be treated as a mixture of two molecular species, and a simple mixture formula be applied to the observed μ^2, a surprisingly low *cis*-content follows : from the experimental values, $\mu = 1{\cdot}2$ or $1{\cdot}6$, the proportions are only *ca.* 9% and 15% respectively. By the same method, an equimolar mixture should correspond to an observed μ as large as 2·9.

It is interesting to compare this result with one obtainable from an entirely different consideration. If the energies of the two forms are E_{cis} and E_{trans}, then the numbers of the molecules N_{cis} and N_{trans} present in solution are given by $N_{cis}/N_{trans} = e^{-dE/kT}$, where dE is the energy difference between the two forms, other symbols having the usual significance. If, as a rough approximation, the energy of each form is written as the potential energy due to the mutual arrangement of the dipolar groupings, then application of the formula

$$U = (\cos \chi - 3\cos \alpha_1 \cos \alpha_2)\mu_1\mu_2/r^3$$

(cf. Jeans, "Electricity and Magnetism," Cambridge University Press, Cambridge, 1920, p. 354) to the above geometrical constructions gives $E_{cis} = 0{\cdot}24876 \,.\, 10^{-12}$ and $E_{trans} = 0{\cdot}19008 \,.\, 10^{-12}$ c.g.s. units, whence $dE = 0{\cdot}05868 \,.\, 10^{-12}$ and $N_{cis}/N_{trans} = 0{\cdot}2375$, or 19% of *cis*-, a figure higher than that deduced experimentally. Nevertheless, although no allowance has been made for a small quantity of a third form, in which the ketone groups are in *cis*-formation at opposite corners of the basal part of the molecule, it is significant that the result is of the same order.

The above discussion is probably slightly erroneous because, owing to impact of solvent molecules, thermal agitation, etc., the state of the solute at any moment is not a mixture of the two extreme forms considered above, but rather a mixture of molecules with configurations intermediate between them. The *observed* moment ($\bar{R}$) therefore is the root mean square of the instantaneous resultant moments which vary during the flexion of the ring. The distribution of the configurations during this process may be supposed at any

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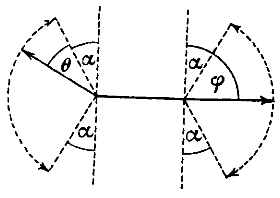
* Assumption of the usual tetrahedral angle leads to a resultant moment for the *cis*-form of 3·95 units, but our conclusions are not appreciably affected if this figure, instead of 4·1, is employed in the calculations.

instant to be governed by the dipolar repulsions between the keto-groups, almost to the exclusion of such factors as the intrinsic energy difference needed to change one form of a saturated non-polar six-ring into the other—the fact that hitherto no separable geometrical isomerides of this type have been confirmed shows that this energy difference is less than that arising from thermal agitation at the ordinary temperatures (*ca.* 600 cals./mol.). These considerations can be summarised in mathematical form :

$$\bar{R}^2 = \frac{\int_{\phi=0}^{\phi=\pi-2a}\int_{\theta=0}^{\theta=\pi-2a}[2\mu^2 + 2\mu^2(\cos\overline{2\alpha+\theta+\phi})]e^{-E/kT}d\theta\,.\,d\phi}{\int_{\phi=0}^{\phi=\pi-2a}\int_{\theta=0}^{\theta=\pi-2a}e^{-E/kT}\,.\,d\theta\,.\,d\phi}$$

where $$E = \frac{\mu^2(\cos\overline{2\alpha+\theta+\phi} - 3\cos\overline{\alpha+\theta}\,.\,\cos\overline{\alpha+\phi})}{\{1{\cdot}52\sqrt{3+2\sin\overline{4^\circ+\theta+\phi}+\sin\overline{\theta+47^\circ}+\sin\overline{\phi+47^\circ}}\}^3}$$

$\alpha = 43^\circ$, $\mu = 2{\cdot}87 = \mu_{C=O}$, and the significances of θ, ϕ, and α are obvious from the inset diagram. A value for $\bar{R}$ of about 1 has been obtained by graphical evaluation of the above integral.

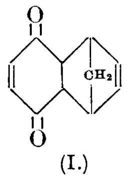


Absence of enolic form in cyclo*hexa*-1 : 4-*dione*. The statements that the aqueous solution is not markedly coloured by the addition of ferric chloride (Herrmann, *Annalen*, 1882, **211**, 322) and that the diketone can be heated for a day with acetic anhydride in an oil-bath at 170° without undergoing acetylation (Baeyer and Noyes, *Ber.*, 1889, **22**, 2177) have been confirmed. The clearest evidence is obtained from a consideration of the molecular refraction values. To explain a moment of the order 1·6 (Hassel) by enolisation this process would have to be fairly complete; now, the observed value for Na_D light is 27·8 (benzene solution) against the calculated values : for the dione, 27·7; for the mono-enol, 28·7; and for the di-enol, 29·7 c.c. (data from Eisenlohr, *Z. physikal. Chem.*, 1910, **75**, 605). The conclusion is, therefore, that the compound is wholly ketonic.

Materials.—The benzene used was purified as described by Le Fèvre and Smith (J., 1932, 2239) with the addition of a final crystallisation immediately before use. *cyclo*Hexadione was obtained from ethyl succinylsuccinate (Meerwein, *Annalen*, 1913, **398**, 248); we also wish to thank Dr. H. G. de Laszlo for the loan of a specimen of this substance. The following measurements relate to benzene solutions.

$f_1 \,.\, 10^6$	0	5010	7114·0	11,989	14,847·9	15,003
$M_1f_1 + M_2f_2$	78	78·170	78·242	78·408	78·505	78·510
ϵ_{25°	2·2725	2·2832	2·2869	2·2975	2·3037	2·3035
d_4°	0·87380	0·87523	0·87588	0·87741	0·87827	0·87833
$P_1f_1 + P_2f_2$	26·5850	26·7575	26·8159	26·9803	27·0767	27·0743
P_2f_2	26·5850	26·4518	26·3958	26·2663	26·1902	26·1861
P_1f_1	—	0·3057	0·4201	0·7140	0·8865	0·8882
P_1 (c.c.)	—	61·0	59·1	59·6	59·7	59·2
n_D	1·49733	—	1·49717	—	1·49703	—
n_D^2	2·24200	—	2·24153	—	2·24109	—
$R_1f_1 + R_2f_2$	26·1357	—	26·1475	—	26·1573	—
R_2f_2	26·1357	—	25·9497	—	25·7475	—
R_1f_1	—	—	0·1978	—	0·4098	—
R_1 (c.c.)	—	—	27·8	—	27·6	—

Whence, extrapolated values of P_1 and R_1 for $f_1 = 0$ are 62 c.c. and 28 c.c. respectively (Clarke, J., 1912, **101**, 1788, using alcoholic solutions, obtained $M_a = 27{\cdot}8$ and $M_\gamma = 28{\cdot}46$ c.c.); $\mu = 0{\cdot}22(34)^{\frac{1}{2}} = 1{\cdot}29$.


(I.)

(b) *Dipole Moment of* cyclo*Pentadienebenzoquinone.*—This compound (I) has an interest in relation to *cyclo*hexadione, for, according to models, the requirements of ring strain must keep the ketonic groups rigidly in a *cis* mutual orientation. Since the observed moment is 1·39, the degree of departure from planarity of the axes of the two carbonyl groups is indicated by the angle (*viz.*, 151°) which a pair of ketone vectors—taken as 2·79 as before—must make with one another to produce this resultant.

This substance was prepared and purified according to Wassermann (this vol., p. 828). The following measurements relate to benzene solutions at 25°.

f_1	0	13,447·7	20,112·9	26,210·9	27,262·5
$M_1f_1 + M_2f_2$	78	79·2910	79·9308	80·5163	80·6172
ϵ	2·2725	2·3112	2·3292	2·3435	2·3451
d	0·87380	0·88152	0·88530	0·88864	0·88925
$P_1f_1 + P_2f_2$	26·5850	27·3566	27·7208	28·0256	28·0646
P_2f_2	26·5850	26·2275	26·0503	25·8882	25·8602
P_1f_1	—	1·1291	1·6705	2·1374	2·2044
P_1	—	83·96	83·06	81·55	80·86
n_D	1·49733			1·49914	1·49040
n_D^2	2·24200			2·24741	2·24712
$R_1f_1 + R_2f_2$	26·1357			26·6099	26·6206
R_2f_2	26·1357			25·4507	25·4232
R_1f_1	—			1·1592	1·1974
R_1	—			44·23	43·92

Whence, extrapolated value of P_1 for $f_1 = 0$ is *ca.* 84 c.c., and ${}_0P = 40$ c.c.

(c) *Dipole Moment of* p-*Benzoquinone.*—Hassel and Naeshagen (*Z. physikal. Chem.*, 1929, *B*, **6**, 445) reported a moment of 0·67 for this substance. The data tabulated below comprise a repetition of this determination. The results with carbon tetrachloride as an alternative solvent show that the magnitude of the earlier result could not have been due to combination with the solvent (benzene), since the ${}_0P$ found in both liquids is *ca.* 10 c.c., corresponding to a moment of the order given by the above authors. On the other hand, since no *diminution* in ${}_0P$ is observable with temperature rise, benzoquinone would appear to be non-polar. The two experimental facts can be harmonised by supposing the solute molecules to be not completely rigid when subjected to the bombardment of the solvent molecules. A finite value for the root mean squares of the instantaneous resultant moments, becoming greater up to a point with temperature increase, would then be expected to arise from the deflexions of the carbonyl groups out of the uniaxial positions given in Fittig's formula. Although similarities exist, the problem cannot be treated so simply as that in Section (a) because the molecule of benzoquinone is undoubtedly much more rigid than that of *cyclo*hexa-1 : 4-dione. The possibility of association of the molecule is negatived by Auwers's molecular-weight determinations (*Z. physikal. Chem.*, 1893, **12**, 698).

Preparation of Materials.—Commercially pure carbon tetrachloride was shaken with sulphuric acid and then washed successively with water, 2*N*-sodium hydroxide, and water. After being dried (sodium sulphate), it was fractionated, the portion of b. p. 78—79° being stored over potash sticks (compare Schmitz-Dumont, *Chem.-Ztg.*, 1897, **21**, 510); after a week it had the following physical constants: $d_{4^\circ}^{25^\circ}$ 1·5844, $n_D^{25^\circ}$ 1·4572; ε_{25° has been taken as 2·2270. The benzene was that used before [Section (b)]. The benzoquinone was a commercial specimen steam-distilled and twice recrystallised from boiling ligroin; m. p. 115·5—116° (cf. Hesse, *Annalen*, 1860, **114**, 300).

Measurements.—The dielectric constants and densities of dilute solutions of quinone in the two solvents named have been measured at 25° and 45°. The refractive indexes (Na light) for two of the benzene solutions have also been observed at the lower temperature. The significant data are collected below.

p-*Benzoquinone in Carbon Tetrachloride Solution.*

$f_1 . 10^6$	0	594·398	1271·91	3523·36	7662·0
$M_1f_1 + M_2f_2$	154	153·9727	153·9413	153·8380	153·6475
		Temperature 25°.			
ϵ	2·2270	2·2278	2·2286$_5$	2·2318	2·2375$_5$
d_{4°	1·5844	1·58445	1·58445	1·58508	1·58623
$P_1f_1 + P_2f_2$	28·214	28·2213	28·2287	28·2506	28·2875
P_2f_2	28·214	28·1972	28·1781	28·1146	27·9978
P_1f_1	—	0·0241	0·0506	0·1360	0·2897
P_1	—	40·58	39·75	38·60	37·81
		Temperature 45°.			
ϵ	2·195	2·1960	2·1968$_5$	2·1999$_5$	2·2058
d_{4°	1·5459	1·54602	1·54605	1·54682	1·54825
$P_1f_1 + P_2f_2$	28·38	28·3873	28·3953	28·4147	28·4501
P_2f_2	28·38	28·3631	28·3439	28·2800	28·1625
P_1f_1	—	0·0242	0·0514	0·1347	0·2876
P_1	—	40·76	40·45	38·24	37·54

Whence, the extrapolated values of P_1 for $f_1 = 0$ are 40·5—41·0 and 41·0—41·1 c.c. at 25° and 45° respectively.

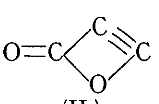
p-*Benzoquinone in Benzene Solution.*

$f_1 . 10^6$	0	5864·3	9763·67	12,458·6	15,534·7
$M_1f_1 + M_2f_2$	78	78·1759	78·2929	78·3737	78·4660
			Temperature 25°.		
ϵ	2·2725	2·2765	2·2793	2·2812	2·2834
$d_{4°}$	0·8738	0·87514	0·87626	0·87693	0·87771
$P_1f_1 + P_2f_2$	26·585	26·6644	26·7113	26·7459	26·78578
P_2f_2	26·585	26·4291	26·3254	26·2538	26·1720
P_1f_1	—	0·2353	0·3859	0·4921	0·6138
P_1	—	40·12	39·53	39·49	39·51
n_D	1·49733	1·497615	—	1·49790	—
n^2_D	2·241997	2·242851	—	2·24370	—
$R_1f_1 + R_2f_2$	26·1356	26·1631	—	26·1925	—
R_2f_2	26·1356	25·9824	—	25·8101	—
R_1f_1	0	0·1807	—	0·3824	—
R_1	0	30·82	—	30·69	—
			Temperature 45°.		
ϵ	2·2330	2·2377	2·2408	2·2427	2·2452
$d_{4°}$	0·8521	0·85374	0·85497	0·85575	0·85661
$P_1f_1 + P_2f_2$	26·664	26·7446	26·7931	26·8255	26·8675
P_2f_2	26·664	26·5076	26·4036	26·3318	26·2498
P_1f_1	—	0·2370	0·3895	0·4937	0·6177
P_1	—	40·40	39·89	39·62	39·76

Whence, extrapolated values of P_1 for $f_1 = 0$ are 40·7 and 40·8 c.c. at 25° and 45° respectively; and that for $[R_L]^{25°}_D$ is 30·9 c.c. (Calc. : 26·93).

From these data : (*a*) substitution of the appropriate figures for 25° in the equation $\mu = 0{\cdot}22({}_0P)^{\frac{1}{2}}$ gives $\mu = 0{\cdot}69$; (*b*) substitution in the equation $P = A + B/T$ of the values of P at 298° and 318° leads to a small negative value for B (*ca.* — 500).

A minor point which emerges from these measurements is the considerable exaltation of molecular refraction, presumably due to the highly conjugated arrangement of bonds, in the benzoquinone molecule.


(II.)

(d) *Dipole Moment of Carbon Suboxide.*—According to classical stereochemistry, Diels and Wolf's formula (*Ber.*, 1906, **39**, 689) for carbon suboxide should correspond to a rectilinear molecule. Brockway and Pauling (*Proc. Nat. Acad. Sci.*, 1933, **19**, 860) reported that electron-diffraction photographs of the gas are not incompatible with such a structure, but Boersch (*Naturwiss.*, 1934, **22**, 172; *Wiener Ber.*, 1935, **144**, 2b, 1), using the same method, concluded that Michael's cyclic representation (II) (*Ber.*, 1906, **39**, 1915) was also admissible.

The data tabulated below are therefore of interest in showing that in benzene solutions very little of the second form can exist, as shown by the facts that the dipole moments of the chain and the ring form should *a priori* be vanishingly small and greater than 3 units respectively, and that the orientation polarisation of a substance with a μ of the latter order must be not less than 186 c.c. at 25° : ${}_0P$ was actually found to be *ca.* 10 c.c.

Materials.—Carbon suboxide, prepared by the pyrolysis of diacetyltartaric anhydride (Hurd and Pilgrim, *J. Amer. Chem. Soc.*, 1933, **55**, 757), was redistilled immediately before use. Solutions were prepared by direct addition of the liquid oxide to previously weighed and frozen quantities of benzene. Errors due to condensation of moisture were avoided by delivering the suboxide through a narrow tube in such a way that no contact with the atmosphere was made. The linear relation between f_1 and d and ε for the solutions was taken as sufficient justification of this simple method.

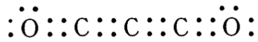
f_1	0	30,102·4	44,354·0	49,987·2	59,970·7
$M_1f_1 + M_2f_2$	78	77·6990	77·5564	77·5001	77·4004
ϵ	2·2725	2·2875	2·2945	2·2972	2·3042
d	0·87370	0·87712	0·87870	0·87938	0·88051
$P_1f_1 + P_2f_2$	26·5894	26·6011	26·6052	26·6040	26·6355
P_2f_2	26·5894	25·7890	25·4100	25·2603	24·9948
P_1f_1	—	0·8121	1·1952	1·3437	1·6407
P_1	—	26·98	26·95	26·88	27·36

Whence, extrapolated value of P_1 for $f_1 = 0$ is *ca.* 27 c.c. The following data are taken from Diels and Blumberg (*Ber.*, 1908, **41**, 86) :

Temp.	*d.*	n_D.	n^2_D.	Mol. refrn.
0°	1·1137	1·45384	2·11367	16·53
− 1·3	1·116	1·45962	2·13049	16·68
−12	1·135	1·46757	2·15376	16·64

From the above data an apparent dipole moment of 0·7 unit is indicated. The magnitude of this result may not be entirely due to experimental errors arising from evaporation or polymerisation of the materials under examination. Of the five most important electronic structures for the Diels–Wolf formula, only the first three are collinear, (iv) and (v) being angular. Resonance between these forms might therefore lead to a finite observable moment. The contributions of the above structures to the normal state of the molecule are in the decreasing order (i > ii . . . . .) of importance given by Brockway and Pauling (*loc. cit.*) ; that nos. (iv) and (v) are not impossible, however, is shown by the course of the many addition reactions in which the suboxide takes part.

(i.)

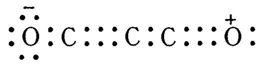


$:\ddot{O}::C::C::C::\ddot{O}:$

(ii.)

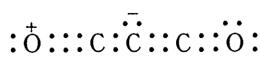
$:\overset{+}{O}:::C:C:::C:\underset{\cdot\cdot}{\overset{-}{\ddot{O}}}:$

(iii.)



$:\underset{\cdot\cdot}{\overset{-}{\ddot{O}}}:C:::C:C:::\overset{+}{O}:$

(iv.)



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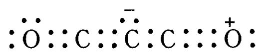
(v.)



$:\ddot{O}::C::\underset{-}{\ddot{C}}:C:::\overset{+}{O}:$

(e) *Dipole Moment of Carbonyl Chloride in Carbon Tetrachloride Solution.*—Saville and Shearer (J., 1925, **127**, 591), from *X*-ray spectra of long-chain aliphatic substances, inferred that the valency angle of the carbonyl group was approximately equal to that of the methane carbon atom, *viz.*, 109—110° ; other workers subsequently suggested that in some cases a larger angle is more correct. The point has some bearing on the matter of the previous sections, and it seemed possible that measurement of the dipole moment of carbonyl chloride might afford relevant information.

Measurements.—The carbonyl chloride was obtained from the commercial toluene solution by warming, etc., as usual, except that, to minimise risk of contamination of the gas with toluene vapour, two double-surface condensers in series, through which cooled water was circulated, were interpolated as a fractionation column; the carbonyl chloride was condensed in a worm cooled in ice–salt, and was once redistilled immediately before the solutions were prepared.

A trial run showed that the last operation could be done accurately enough by weight. The solvent used was that purified as detailed on p. 1698. Known weights (*ca.* 50 g.) of this, contained in glass-stoppered flasks, were immersed in a freezing-mixture until cooled to below 0°. The carbonyl chloride was then distilled and introduced from an extension tube on the worm as a liquid just above the carbon tetrachloride surface; after short standing, to reach a temperature above the dew-point, the flasks were reweighed. The weights of solute were thus obtained with sufficient accuracy to make quantitative analysis of the solutions unnecessary.

Measurements of density, refractive index, and dielectric constant were made as before. We found $\mu = 1{\cdot}099$, whereas Smyth and McAlpine (*J. Amer. Chem. Soc.*, 1934, **56**, 1697) record 1·18 for the gas. The details are tabulated below, the value of ε for liquid carbonyl chloride ($f_1 = 1$) being that of Schlundt and Germann (*J. Physical Chem.*, 1925, **29**, 353). This, combined with a density value calculated from our data by application of the mixture law, leads to a figure for the total polarisation which is slightly lower than that obtained at infinite dilution in carbon tetrachloride solutions.

Molecular Polarisation and Refractivity of Carbonyl Chloride in Carbon Tetrachloride at 0°.

$f_1 . 10^6$.	$M_1f_1 + M_2f_2$.	ε.	$d^{0°}_{4°}$.	$P_1f_1 + P_2f_2$.	P_2f_2.	P_1f_1.	P_1, c.c.
0	154	2·2748	1·6317	28·116	28·116	—	—
9,302·3	153·488	2·28702	1·63019	28·2661	28·8544	0·4117	44·25
13,930·3	153·234	2·29378	1·62944	28·3373	27·7243	0·6130	44·00
15,469·6	153·149	2·29615	1·62919	28·3609	27·6811	0·6798	43·95
17,007·0	153·065	2·29844	1·62894	28·3844	27·6378	0·7466	43·90
20,077·0	152·896	2·30297	1·62844	28·4308	27·5515	0·8793	43·80
60,869·0	150·652	2·35599	1·62171	28·9185	26·4046	2·5139	41·30
90,322·0	149·032	2·38735	1·61676	29·1487	25·5765	3·5722	39·55
10^6	99	4·724	1·414	38·77	—	38·77	38·77

Whence, P_1 at infinite dilution = 44·7 c.c.

$f_1 \cdot 10^6$	n_D.	n^2_D.	$R_1f_1 + R_2f_2$.	R_2f_2.	R_1f_1.	R_1, c.c.*
0	1·47161	2·16564	26·41	26·41	—	—
9,302·3	1·46908	2·15821	26·2253	26·1643	0·06093	17·3
13,930·0	1·47089	2·16351	26·2803	26·0421	0·2382	17·1
17,007·0	1·47084	2·16337	26·2570	25·9608	0·2962	17·3

Whence, R_D at infinite dilution = 17·4 c.c.

$$\mu = 0{\cdot}21033\sqrt{44{\cdot}7 - 17{\cdot}4} = 0{\cdot}21033\sqrt{27{\cdot}3} = 1{\cdot}099.$$

* *R*, calc. for Na light = 17·3 (cf. *Z. physikal. Chem.*, 1910, **75**, 603).

The dipole moment of carbonyl chloride must be the resultant compounded from that of the ketone group and those of the two C–Cl linkings. If μ_{CO} is taken as lying between 2·75 and 3·00 (Wolf, *Z. physikal. Chem.*, 1928, *B*, **2**, 39; Wolf and Gross, *ibid.*, 1929, *B*, **4**, 305) and μ_{CCl} as 1·86 (*i.e.*, as μ_{MeCl}; Sänger, *Helv. Physica Acta*, 1930, **3**, 161), the Cl–C–Cl angle, θ, is calculable from $\mu_{CO} - 2\mu_{CCl} \cos \theta/2 = \mu_{COCl_2}$ as θ = 127—119°. No great accuracy can be expected in such an estimate because no means are at present available to effect corrections for mutual induction and the consequent departure from vector additivity. It is, however, noteworthy that by equating the difference between μ_{Me_2CO} and $\mu_{CH_3 \cdot COCl}$ to $\cos \theta/2 \cdot \mu_{MeCl}$, and taking the dipole moment of acetyl chloride as 2·7 (Zahn, *Physikal. Z.*, 1932, **33**, 686), a value for θ of the same order is obtained, *viz.*, 115°. The present value can be regarded as a probable upper limit for the angle between the remaining two valencies of a keto-carbon atom, and is to be compared with the following estimates: 120° (Becker and Thorpe, *loc. cit.*), 109—110° (Saville and Shearer, *loc. cit.*), 110° ± 5° (Dornte, *J. Amer. Chem. Soc.*, 1933, **55**, 4126), and 115° (see above). It is probable from the order of the angle that ketone-containing molecules are of the valency force type and could easily undergo distortion by, *e.g.*, the spatial requirements of component groups. Such an explanation for the size of the carbonyl chloride angle was at first sight attractive because Bewilogua (*Physikal. Z.*, 1930, **31**, 265), using the *X*-ray method, had found 124° for the Cl–C–Cl angle in methylene chloride. Two sets of facts militate against the likelihood of such a steric effect being operative: (1) Dornte (*J. Chem. Physics*, 1933, **1**, 566, 630) has found that methylene dibromide and di-iodide *also* have angles of 125° ± 5°, notwithstanding the increase of the diameter of the halogen atom involved from 2 Å. to 2·7 Å.; (2) inspection of scale drawings on the basis that the radii of the carbon and the chlorine atom are 0·76 and 1·0 Å. respectively (Goldschmidt, *Trans. Faraday Soc.*, 1929, **25**, 282), and that the chlorine atoms are surrounded by an impenetrable envelope *ca.* 0·5 Å. thick (Sidgwick, "The Covalent Link in Chemistry," Cornell Univ. Press, 1933, p. 233), shows clearly that the Cl–C–Cl angle can be as small as 117° and yet conform to the above postulates.

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