252. *Studies in Dielectric Polarisation. Part XVIII. The Dipole Moments of the Chlorides of Some Dicarboxylic Acids.*

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SINCE both the magnitude and direction of the COCl group moment have been exactly determined (Part XVI, this vol., p. 158) from the moment of acetyl chloride and of trichloroacetyl chloride, it was considered that a determination of the moments of compounds containing two of these groups would be of interest in relation to the configuration of the carbon chains in aliphatic compounds and the possibility of free rotation about the C—C bonds. The possibility of isomerism in some of these compounds might also be decided.

The moments of oxalyl, malonyl, and succinyl chlorides have therefore been measured in benzene solution. It is known that substances such as dichloroethane, in which rotation of polar groups can occur, have large dipole moments when measured in benzene solution (Meyer, *Z. physikal. Chem.*, 1930, *B*, **8**, 27; Müller, *Physikal. Z.*, 1933, **34**, 709; Stearn and Smyth, *J. Amer. Chem. Soc.*, 1934, **56**, 1667). The moment of dichloroethane in benzene is larger than that found for the vapour, and indicates considerable deviation from the *trans*-position. The result for the moment of oxalyl chloride in benzene solution does not appear to show such abnormal behaviour, and this probably holds for other compounds containing the COCl group.

For succinyl chloride the possibility of a lactone form arises, but previous physical measurements (which are discussed later) have shown that in the liquid this form does not exist. Phthalyl chloride, on the other hand, is known to exist in two forms, a stable form, m. p. 13°, and an unstable form, m. p. 88·5°. From both chemical and physical evidence it has been concluded that the solid form is the asymmetric one, while the low-m. p. form is symmetrical. The dipole moment of the symmetrical (acyclic) form has now been measured and it is proved that the liquid form has the symmetrical formula; since the preparation of the asymmetric form in a pure state is a difficult and somewhat lengthy operation, its dipole moment was not measured.

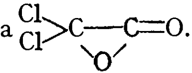
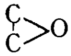
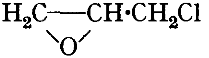
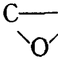
The values of the dipole moments found are as follows (all in Debye units in benzene solution at 20°):

Oxalyl chloride	0·92	Succinyl chloride	3·00
Malonyl chloride	2·80	*s*-Phthalyl chloride	5·12

The moment of oxalyl chloride is small, as would be expected if it has a symmetrical structure. If each COCl group is assumed to have a moment of 2·45 (the moment of acetyl chloride in benzene solution) acting at an angle of 16° to the direction of the C—C axis, then the following values of the moment can be calculated:

Molecule fixed with O atoms in *trans*-position	0
,, ,, ,, ,, *cis*- ,,	1·16
Free rotation about C—C bond	0·95

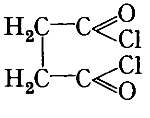
The value for free rotation is calculated by the method described by Zahn (*Physikal. Z.*, 1932, **33**, 400). The observed value of 0·92 can therefore be explained by either free rotation or oscillation about the stable *trans*-position.

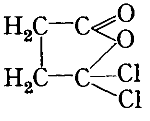
Froschl, Maier, and Heuberger (*Monatsh.*, 1932, **59**, 256) examined the compounds formed by reduction of oxalyl, malonyl, and succinyl chlorides, and concluded that whereas malonyl chloride has the normal structure, oxalyl chloride has an unsymmetrical structure and succinyl chloride consists of a tautomeric mixture of two forms with normal and lactone structures. From oxalyl chloride neither glyoxal nor glyoxylic acid could be obtained, while the production of carbonyl chloride indicated that both chlorine atoms were attached to the same carbon atom, as in the formula  $\begin{matrix}Cl\\Cl\end{matrix}\!>\!\underset{\searrow O\swarrow}{C\!-\!\!-\!C}\!=\!O$. It might be supposed that the low value of the dipole moment as well as of the dielectric constant of oxalyl chloride (3·470; Pyle, *Physical Rev.*, 1931, **38**, 1065) would point to the symmetrical structure, but the unsymmetrical formula given above would also have a small moment. This can be considered as the resultant of the  $\begin{matrix}C\\C\end{matrix}\!>\!O$, C═O, and CCl_2 moments acting at 120° to each other, all outwards from the ring. Taking for these the moments of ethylene oxide (1·88, Stuart, *Z. Physik*, 1928, **51**, 502), *cyclo*hexanone (2·8 in benzene; Williams, *J. Amer. Chem. Soc.*, 1930, **51**, 1833), and methylene chloride (1·61 in benzene; Mahanti and Das Gupta, *J. Indian Chem. Soc.*, 1929, **6**, 411), the resultant is found to be 1·1. Although the value observed for the dipole moment in benzene solution, 0·92, is smaller than this, the difference is small. The unsymmetrical structure therefore cannot be definitely excluded by the value of the dipole moment. In this connexion use can be made of the refractivity. If the refractivity of the COCl group is taken as 11·09 for the D line (from the value 16·81 for acetyl chloride, Part XVI, *loc. cit.*), the calculated refractivity for oxalyl chloride is 22·18, while that calculated for the unsymmetrical structure (sum of atomic refractions) is 22·56. For epichlorohydrin  $\underset{\searrow O\swarrow}{H_2C\!-\!\!-\!CH}\cdot CH_2Cl$ the observed molecular refractivity is 20·57 (20·56, Brühl, *Ber.*, 1891, **24**, 661; 20·58, Walden, *Z. physikal. Chem.*, 1907, **59**, 401) and the calculated value is 20·37. If the difference of 0·20 is an exaltation due to the  $\underset{\searrow O\swarrow}{C\!-\!\!-\!C}$ ring, it should also be present in the unsymmetrical form of oxalyl chloride, the refractivity of which should therefore be 22·76. The observed value 22·25 agrees better with the symmetrical formula, and may be a little high, since the rapid hydrolysis of this compound may make the density slightly low. Evidence for the symmetrical formula is also provided by electron-diffraction measurements on the vapour (Wierl, *Physikal. Z.*, 1930, **31**, 366), which indicate the existence of molecules with varying Cl—Cl distances, due to intramolecular rotation. The physical evidence therefore seems to exclude the unsymmetrical structure.

For malonyl chloride, rotation could occur about the two C—C bonds, and from a calculation by Zahn's method the results obtained are : free rotation 2·83 ; fixed, minimum 1·62 ; fixed, maximum 3·86. The observed moment (2·80) is therefore in good agreement with that calculated for free rotation of both the COCl groups. The introduction of the CH_2 group would be expected to reduce the interaction between them.

Succinyl chloride was at one time thought to consist of a mixture of the two forms (I) and (II). Auger (*Bull. Soc. chim.*, 1888, **49**, 345) arrived at this conclusion from an examination of its chemical reactions, but, according to Morrell (J., 1914, **105**, 1733) all the chemical reactions can be explained by the symmetrical formula (I) and there is no reason to believe that the form (II) exists. Ott (*Annalen*, 1912, **392**, 245) from molecular volume determinations, and von Auwers and Schmidt (*Ber.*, 1913, **46**, 472) from refractivity measurements, concluded that succinyl chloride existed only in the symmetrical form. Garner and Sugden (J., 1927, 2877) found the parachor to be in excellent agreement with the value calculated for the symmetrical formula, so that it can be assumed that, in the liquid, only the symmetrical form (I) exists.

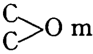
(I.)





(II.)

Calculation of the moment of succinyl chloride by Zahn's method, assuming free rotation about all the bonds, gives a value of 3·28. Since the observed value 3·00 is a little less than this, it seems that rotation is not completely free. Gane and Ingold (J., 1931, 2153) from calculations based on the dissociation constants of dicarboxylic acids, and Ingold (*ibid.*, p. 2170) from the rates of hydrolysis of dicarboxylic esters, concluded that the carbon chain has a rigid extended configuration, while Smyth and Walls (*J. Chem. Physics*, 1933, **1**, 200), from measurement of the moments of a series of polymethylene bromides, concluded that the carbon chain was a rigid zig-zag but the polar groups at the ends could rotate. For such a structure in succinyl chloride, even if the COCl groups could rotate freely about the bonds joining them to the inner carbon atoms, the value of the moment would be the same as that calculated for oxalyl chloride, *i.e.*, 0·95. The large value 3·00 indicates that the carbon chain cannot be planar and rigid, and that considerable flexibility, approaching completely free rotation, is possible. It must be borne in mind, however, that this result may be affected by the solvent.

The symmetrical structure of succinyl chloride is confirmed by the dipole-moment measurement. The lactone form, if it existed, would have a much smaller moment, since the C═O and the CCl_2 moment would oppose each other. If these are taken, as before, to be 2·8 and 1·61 then, although they do not act in exactly opposite directions, the resultant would probably be about 1·5. If the  $\overset{C}{\underset{C}{}}\!>\!O$ moment is taken as that of tetrahydrofuran in benzene (1·71 ; Smyth and Walls, *J. Amer. Chem. Soc.*, 1932, **54**, 3234), these two moments, both acting outwards from the ring at an angle of about 108° to each other, would give a resultant of 1·9, which is much less than the observed value 3·00. There is no physical evidence to indicate that succinyl chloride exists in the asymmetrical form.

Phthalyl chloride exists in two forms, a solid form, m. p. 83·5°, and a liquid form, m. p. 13°. The solid form is considered to have the asymmetric or cyclic structure. In this connexion it is interesting to note that phthalyl fluoride exists only in the acyclic form, as indicated by parachor measurements and its rate of reaction with *iso*propyl alcohol and aniline (Dann, Davies, Hambly, Paul, and Semmens, J., 1933, 15). Phthalyl bromide exists in two forms, which are tautomeric. The cyclic form is solid at ordinary temperature, but on melting is converted into the acyclic form, the reverse change occurring slowly on cooling. The two can be distinguished by the great difference in their rates of reaction with *iso*propyl alcohol, while the parachor of the liquid form at a temperature above the m. p. indicates that it has the acyclic structure (Davies, Hambly, and Semmens, *ibid.*, p. 1309).

The molecular refractivity of the liquid phthalyl chloride (Brühl, *Annalen*, 1886, **235**, 13; von Auwers and Schmidt, *loc. cit.*, p. 483) indicated that it had the symmetrical formula. Ott (*loc. cit.*) discovered the asymmetric form and concluded from molecular volume measurements that the liquid form has the symmetrical structure. Pfeiffer (*Ber.*, 1922, **55**, 413) was able, by chemical reactions, to confirm this result, while parachor determinations (Garner and Sugden, *loc. cit.*) on both forms support this conclusion, although the parachors for each compound did not agree exactly with the values calculated for them.

The large value (5·12) for the dipole moment of the liquid form of phthalyl chloride indicates that it has the symmetrical formula, since for the cyclic form a comparatively small moment, of the same order as that calculated for the hypothetical lactone form of succinyl chloride, would be expected. For the position of minimum moment, with the C═O groups directed away from each other, the two COCl moments would act at an angle of 92° to each other, giving a resultant of 4·63. The moment of the COCl group in this compound is assumed to be the moment of benzoyl chloride in benzene, 3·33 (Part XVII). It is generally found that the moment of an *o*-disubstituted benzene is smaller than that calculated by vector addition, an angle of 60° being assumed between the two moments. The large value (5·12) for the moment of *s*.-phthalyl chloride proves conclusively that it contains two COCl groups. The fact that it is larger than the calculated value shows that some rotation of the COCl groups from the position of minimum moment must occur.

EXPERIMENTAL.

The apparatus and method of calculation were the same as in the previous paper.

Materials.—The benzene used as solvent was the same as that used previously.

Oxalyl chloride (Kahlbaum) was twice fractionated and fractionally frozen. Malonyl chloride (Fraenkel and Landau) was twice fractionated under reduced pressure. Succinyl chloride and phthalyl chloride (Kahlbaum) were fractionated under reduced pressure and fractionally frozen.

The physical constants found were as follows :

Compound.	B. p.	M. p.	$D_{4°}^{20°}$.	$n_D^{20°}$.	$[R_L]_D$.
Oxalyl chloride	61·1°/743 mm.	−10·0°	1·4785	1·4316	22·25
Malonyl chloride	53·6/22	—	1·4509	1·4639	26·79
Succinyl chloride	78·6/11	17·7	1·3748	1·4683	31·34
s-Phthalyl chloride	153·3—153·7/22	11·5—12	1·4060	1·5692	47·31

Figures for comparison are :

Oxalyl chloride : b. p. 63·5—64°/763 mm., m. p. − 12° (Staudinger, *Ber.*, 1908, **41**, 3563); $D_{4°}^{13·4°}$ 1·4884, $n_D^{12·9°}$ 1·434 (von Auwers and Schmidt, *ibid.*, 1913, **46**, 477). Malonyl chloride : b. p. 53—54°/19 mm., $D_{4°}^{22·9°}$ 1·4505, $n_D^{22·1°}$ 1·462 (*idem, ibid.*). Succinyl chloride : b. p. 88·8°/19 mm., $D_{4°}^{15·2°}$ 1·3948, $n_D^{15·2°}$ 1·473 (*idem, ibid.*); m. p. 17° (Purvis, Jones, and Tasker, J., 1910, **97**, 2289). *s*.-Phthalyl chloride : m. p. 11—12° ("Organic Syntheses," Vol. 11, p. 88); b. p. 156—157°/23 mm., $D_{4°}^{15·2°}$ 1·4081, $n_D^{15·5°}$ 1·571 (von Auwers and Schmidt, *loc. cit.*); $D_{4°}^{20°}$ 1·4089, $n_D^{20°}$ 1·5692 (Brühl, *Annalen*, 1886, **235**, 13).

Results.—Solvent, benzene. All measurements at 20°.

Oxalyl chloride.

f_2.	$D_{4°}^{20°}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	0·8791	2·279	26·54	—
0·02149	0·8909	2·299	26·83	39·9
0·04350	0·9025	2·319	27·13	40·0
0·06521	0·9150	2·341	27·43	40·2
0·08360	0·9255	2·356	27·66	39·9

$P_{2\infty}$ = 40·0 c.c.; P_E = 22·2 c.c.; μ = 0·92.

Malonyl chloride.

f_2.	$D_{4°}^{20°}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	0·8790	2·277	26·51	—
0·01334	0·8878	2·424	28·67	188·4
0·02344	0·8943	2·537	30·22	185·0
0·03596	0·9027	2·676	32·03	180·0
0·04691	0·9099	2·798	33·55	176·6

$P_{2\infty}$ = 192·3 c.c.; P_E = 26·8 c.c.; μ = 2·80.

Succinyl chloride.

f_2.	$D_{4°}^{20°}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	0·8791	2·279	26·54	—
0·01479	0·8881	2·472	29·35	216·4
0·02880	0·8970	2·659	31·86	211·1
0·04314	0·9057	2·855	34·33	207·0
0·05693	0·9144	3·038	36·46	200·8

$P_{2\infty}$ = 222·1 c.c.; P_E = 31·3 c.c.; μ = 3·00.

s-Phthalyl chloride.

f_2.	$D_{4°}^{20°}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	0·8792	2·280	26·55	—
0·01029	0·8879	2·669	31·94	550·4
0·02032	0·8965	3·048	36·47	515·0
0·03037	0·9048	3·431	40·49	485·6
0·04003	0·9128	3·796	43·90	460·0

$P_{2\infty}$ = 603·0 c.c.; P_E = 47·3 c.c.; μ = 5·12.

SUMMARY.

The dipole moments of oxalyl, malonyl, and succinyl chlorides have been measured, and the results discussed in relation to the spatial configuration of the COCl groups. For oxalyl and succinyl chlorides the possibility of isomeric ring forms is discussed. The dipole moment of the liquid form of phthalyl chloride is shown to confirm its symmetrical structure.

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