32. *Studies in Dielectric Polarisation. Part XVI. The Dipole Moments of Some Acid Halides and of Phosphorus Oxychloride.*

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ZAHN (*Physikal. Z.*, 1932, **33**, 686) measured the dipole moments of acetyl and chloroacetyl chlorides in the vapour state; the value found for the former, *viz.*, 2·68 (all values here and throughout are in Debye units), is in good agreement with that, 2·70, calculated by Højendahl (Thesis, Copenhagen, 1928, p. 128) from Pohrt's data (*Ann. Physik*, 1913, **42**, 569)—the values calculated from these data are generally too high. The moments of acetyl chloride and bromide and of propionyl, *n*-butyryl, *n*- and *iso*-valeryl chlorides have now been measured in benzene solution. The only possible impurity in the acid chlorides is a slight trace of phosphorus oxychloride remaining from the preparation, and the dipole moment of this compound was measured in order to ascertain if its presence would have any appreciable effect on the results. Since the moment found for chloroacetyl chloride in benzene solution was greater than that found by Zahn for the vapour state, it was measured again in carbon disulphide solution, and a value lower than that in the vapour state was found. The moment of trichloroacetyl chloride was measured in order to determine the direction of the $^-$COCl group moment.

The following values of μ have been found (all in benzene at 20°, unless otherwise stated) :

Acetyl chloride	2·45	Acetyl bromide	2·43
Propionyl chloride	2·61	Chloroacetyl chloride	2·22
n-Butyryl chloride	2·61	Chloroacetyl chloride (in CS_2)...	2·06
n-Valeryl chloride	2·61	Trichloroacetyl chloride	1·19
*iso*Valeryl chloride	2·63	Phosphorus oxychloride	2·40

The value 2·45 for acetyl chloride in benzene solution is considerably lower than that found in the vapour state, *viz.*, 2·68 and 2·70 (see above). This is a normal general result, but, in this case, the difference is larger than is usually found between the moments in the vapour state and in solution in benzene for a moment of this size; the values for acetone, *e.g.*, are : vapour 2·85 (Zahn, *loc. cit.*), solution 2·76 (Wolf and Gross, *Z. physikal. Chem.*, 1931, *B*, **14**, 305).

The value 2·68, which had been accepted as the moment of acetyl chloride, is considerably larger than that calculated from the C═O and the C—Cl moment (see Zahn, *loc. cit.*; Smyth and McAlpine, *J. Amer. Chem. Soc.*, 1934, **56**, 1697). These authors suggest that the high value can be explained by deformation of the tetrahedral symmetry of the molecule, this causing a reduction of the angle between the two moments. Dornte (*ibid.*, 1933, **55**, 4126), by electron-diffraction measurements, has found the C—C—Cl angle in acetyl chloride to be 110° ± 10°, which, if the valencies are assumed to be symmetrical, gives a value for the Cl—C=O angle of 125° ± 10°. Smyth and McAlpine have shown that the value 2·68 for acetyl chloride can be explained in this way only on the assumption of the much smaller angle of 114·5°. We regard such a low value as improbable. Sutton (*Trans. Faraday Soc.*, 1934, **30**, 795), by taking the C=O moment as that of acetone, 2·75 (Wolf and Gross, *loc. cit.*), and the C—Cl moment as that of *tert.*-butyl chloride, 2·15 (Parts, *Z. physikal. Chem.*, 1930, *B*, **7**, 327; cf. van Arkel and Snoek, *ibid.*, 1932, *B*, **18**, 159)—both from measurements in solution—and the angle between them as 125°, calculates the moment of acetyl chloride to be 2·3. An examination of the vector diagram for the acetyl chloride molecule shows that a variation in the value taken for the C—Cl moment affects only slightly the magnitude of the resultant, but causes considerable variation in its direction. In order to calculate the moment of acetyl chloride, Smyth and McAlpine used for the C=O moment that of acetone (Zahn, *loc. cit.*; Stuart, *Z. Physik*, 1928, **51**, 490), and for the C—Cl moment that of methyl chloride, 1·86 (Sänger, *Helv. Phys. Acta*, 1930, **3**, 161; Fuchs, *Z. Physik*, 1930, **63**, 824), both determined in the vapour state. These two components acting at an angle of 125° to each other give a resultant of 2·35 acting at an angle of 15° to the C—C axis. A similar value can be calculated from solution measurements. Morgan and Lowry (*J. Physical Chem.*, 1930, **34**, 2385) find the moment of methyl chloride in carbon tetrachloride solution to be 1·65; the moment in benzene solution can therefore be assumed to be 1·7. A calculation similar to the above gives a resultant of 2·25 acting at an angle of 16° to the C—C axis. This angle is of importance in the calculation of the moments of chloroacetyl and trichloroacetyl chloride, which are discussed below.

The moment of propionyl chloride, 2·61, is greater than that of acetyl chloride, but the moment then remains constant as the homologous series is ascended. The induction which occurs in this series does not, therefore, extend beyond the second carbon atom in the chain, a result in accordance with that found by Cowley and Partington (Part XIII, J., 1935, 604) for the aliphatic nitriles and with that found for the alkyl halides (*ibid.*, Table III; also Mahanti, *Phil. Mag.*, 1935, **20**, 274). Although insufficient data for aldehydes are available to allow any conclusions to be drawn, Wolf and Gross (*loc. cit.*) found that the moments of many ketones are approximately equal. The induction effect, therefore, appears to depend on the presence of the C—Cl moment. The discrepancy between the calculated moment, 2·25, and the observed one, 2·45, for acetyl chloride in solution cannot be completely explained by assuming an action of the C=O moment on the C—Cl moment, or *vice versa*, and is probably due to the neglect of the effect of induction. That the COCl group exerts a powerful inductive effect is shown by the increase in moment from acetyl to propionyl chloride. This is probably a consequence of the action of the moment almost along the direction of the chain. It is, therefore, possible that the high value for the moment of acetyl chloride is due to induction in the C—C bond.

Dornte (*loc. cit.*) has found the Br—C—C angle in acetyl bromide to be 110° ± 10°, so if we apply the same argument to this compound, the moment should be almost identical with that of acetyl chloride. It is found to be 2·43, as compared with 2·45 for acetyl chloride. This small difference probably results from the fact that the C—Br moment is less than the C—Cl moment. The moment decreases in the series methyl chloride, bromide, iodide (see Table III, Part XIII, *loc. cit.*). For acetyl iodide, $P_{2\infty}$ was found to be 131 c.c., and by assuming the value 26·1 c.c. for P_E (Gustus and Stevens, *J. Amer. Chem. Soc.*, 1933, **55**, 374), the moment is calculated to be 2·22. The ease with which this compound decomposes renders the experimental result less accurate than the others, so that it is not entered in the table, but the compound would be expected to have a smaller moment than acetyl bromide, since the C—I moment is less than the C—Br moment.

The moments of chloroacetyl chloride in benzene (2·22) and in carbon disulphide (2·06) may be compared with the value (2·18) found for the vapour by Zahn, and suggest that his value may be a little too low. He found that this moment did not vary appreciably with temperature, a result which was explained by the fact that the COCl and the C—Cl moment acted almost at right angles, which was shown by the vector diagram. Rotation about the C—C bond would not appreciably affect the moment. Application of Zahn's method (*Physikal. Z.*, 1932, **33**, 400) for the calculation of the dipole moments of molecules containing axes of rotation, on the assumption that the values of the COCl and the C—Cl moment are 2·45 and 1·70, respectively, gives the result 2·47. Since the observed value is 2·22, free rotation obviously does not occur. The minimum value of the moment was calculated as 2·05. It seems, therefore, that oscillations about the position of minimum moment occur.

In the calculation of the moment of trichloroacetyl chloride, it will first be assumed that the COCl moment acts at an angle of 15° to the direction of the C—C axis. The CCl_3 moment obviously acts along this axis but in the opposite direction. The COCl moment is taken as that of acetyl chloride, *viz.*, 2·45, and that of CCl_3 as that of methylchloroform, 1·57 (Sutton, *Proc. Roy. Soc.*, 1931, **133**, 668). These two moments acting at an angle of 165° to each other give a resultant of 1·1. If the COCl moment is assumed to act at an angle of 16° to the direction of the C—C axis, the result is 1·2, in good agreement with the observed value, 1·19. The value 16° is confirmed by the angle calculated from the moments of benzoyl chloride and *p*-nitrobenzoyl chloride, the results for which, together with those for other substituted benzoyl chlorides, will shortly be published.

The moment of phosphorus oxychloride, 2·40, can be regarded as the difference between the $P \longrightarrow O$ and the PCl_3 moment, since these act in opposite directions. The moment of phosphorus trichloride was found by Smith (*ibid.*, 1932, **136**, 251) to be 1·16 in benzene solution (P_E being determined by the optical method). From this, the $P \longrightarrow O$ moment is found to be 3·56, which is of the right order for a semipolar link between the phosphorus and the oxygen atom.

EXPERIMENTAL.

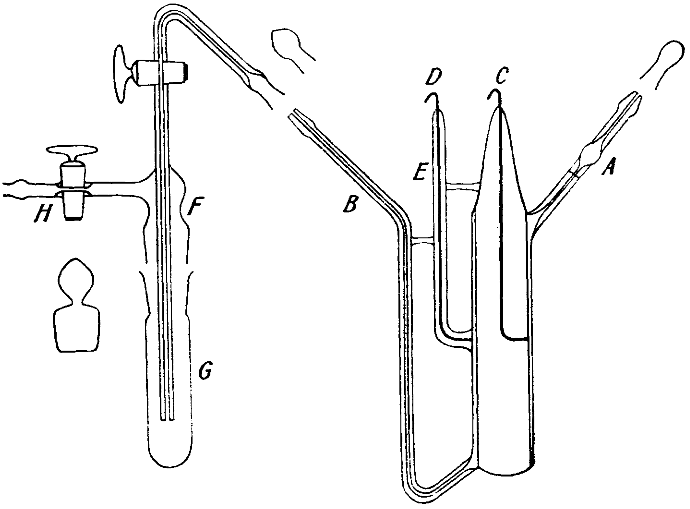
The dielectric constants were measured by means of the apparatus described in Parts XII and XIII (J., 1935, 602, 604). The dielectric cell is similar to that used in Part XII. It consists of two concentric glass cylinders sealed together at the top and bottom, with a separation of 1 mm., both ends of the inner one being sealed. Capillary tubes are sealed in at the top and bottom, as indicated in the figure. Liquid is introduced through the tube *B*, and the tube *A* has a mark and small expansion bulb, so that the complete cell resembles a single-bulb pyknometer. The ends of the tubes *A* and *B* are fitted with ground-glass caps, and the cell is of such a size that it can be conveniently weighed on an ordinary balance for determination of densities. The plates consist of silver coatings deposited on the glass, contact being made with them by stout platinum wires sealed through the walls. The wire (*C*) from the inner plate passes up through the inner glass cylinder, which extends past the outer one, and is sealed through the top of the cell. The wire (*D*) from the outer plate is protected by a glass tube *E*, which runs parallel with the filling tube *B*, and is sealed at the top. These two platinum wires are bent over and dip into mercury cups on the screened lead from the standard condenser. Since the outer plate is earthed, no screening is necessary. The cell is supported in a water thermostat maintained at 20° ± 0·05°. The water level in the thermostat was kept constant, but within limits of ¼ inch the capacity of the cell was scarcely altered. The cell was connected with the standard condenser by lowering it through about 0·5 mm. so that the platinum wires dipped into the mercury cups. This was done by a spring-loaded screw mechanism clamped firmly to two rigid metal bars, the ends of which were fixed to the sides of the thermostat.

The whole of the inside of the cell was silvered to within a short distance of the top, this silver deposit being continuous. The silvering solution contained glucose as reducing agent (Sugden, J., 1933, 768). To obtain two separate plates, the silver was removed for a short distance at the bottom by means of a dilute chromic acid solution (0·5 g. $K_2Cr_2O_7$, 15 c.c. water, 10 drops conc. H_2SO_4), which was found to give good results and did not render the edges of the remaining silver liable to come away from the glass on washing with water. After removal of the acid, the cell was well washed with distilled water, dried by a current of air, and washed with the pure benzene used as solvent. Its volume was also determined by means of benzene, the density of which had been accurately determined. The capacity of the cell is 60 $\mu\mu$F, and its volume 9·4 c.c.

The densities of the solutions were determined to within 0·0001 by means of the cell, and those of the pure substances by a 10 c.c. pyknometer, all at 20° ± 0·05°. The refractive indices were determined with a Pulfrich refractometer at the same temperature.

The symbols and method of calculation are the same as in previous parts of the series, the atomic polarisation being, as usual, left undetermined.

Preparation and Measurement of Solutions.—All possible precautions were taken to exclude moisture during the preparation and measurement of the solutions, since all the compounds are very readily hydrolysed. The solutions were prepared in glass vessels with ground-glass stoppers, one of which (*G*) is shown in the figure. The ground joints at the top of each vessel were interchangeable, so that all the vessels could fit a hollow stopper (*F*) through which a capillary passed. One end of the capillary dipped to the bottom of the vessel, and the other had a ground joint fitting the dielectric cell. A tap just above the stopper cut off the flow of liquid when the cell was full. The solutions were blown into the cell by a stream of dry air passed through a tube (*H*), fitted with a tap, sealed into the hollow stopper on to which the vessels fitted.



When a specimen of the compound having a constant b. p. had been obtained by fractionation, and its physical constants determined, it was distilled from a column with the condenser passing into a Brühl receiver, of the type used for vacuum distillation, which was closed by a calcium chloride tube. The carefully dried and weighed filling vessels were supported in holes in the rotating disc, so that the distillate could be collected in each vessel in turn, the amounts being estimated by counting the drops. The stoppers were then quickly inserted and the vessels removed from the receiver and weighed. 13 C.c. of dry benzene were poured quickly into each vessel from a measuring cylinder, the stoppers being removed for the shortest possible time. The vessels were then reweighed. The solutions were kept in a desiccator, and used as soon as possible after preparation. When they were being introduced into the cell, the stopper of the vessel was removed and quickly substituted by the hollow stopper carrying the filling tube, the solution being then blown into the cell. The capacity of the cell was measured as soon as the solution had reached the temperature of the thermostat. The interval of time required was reduced by keeping both the cell and the vessel containing the solution in the thermostat for some time before filling the cell. The capacity of the cell filled with a solution remained constant for several hours, except in the case of acetyl bromide and, to a less extent, acetyl chloride, where slight changes were detected after a time. When the capacity of the cell became constant, the liquid was adjusted to the mark, the cell removed from the thermostat, and its outside carefully dried. After attaining the temperature of the balance case, it was weighed.

Preparation of Materials.—Acetyl chloride and bromide, *n*-butyryl chloride, and chloroacetyl chloride were obtained from Kahlbaum and fractionated twice; *iso*valeryl chloride (Kahlbaum) was thrice fractionated. Propionyl and trichloroacetyl chlorides (Fraenkel and Landau) were fractionated twice.

n-Valeryl chloride was prepared from *n*-valeric acid previously fractionated twice; b. p. 185—186°/768 mm. The acid was treated with a slight excess of phosphorus pentachloride and distilled, the *n*-valeryl chloride being isolated from the mixture by fractionating it four times through a very efficient column. Phosphorus oxychloride (Kahlbaum) was twice fractionated and then fractionally frozen.

The physical constants of the materials used are given below :

Compound.	B. p.	$D^{20°}_{4°}$.	$n^{20°}_{D}$.	$[R_L]_D$.
Acetyl chloride	50·6°/756 mm.	1·1044	1·3887	16·81
Propionyl chloride	78·3°/766	1·0565	1·4038	21·40
n-Butyryl chloride	101·5°/768	1·0205	1·4126	26·00
n-Valeryl chloride	126·9°/756	1·0004	1·4207	30·53
*iso*Valeryl chloride	115·5°/741	0·9862	1·4157	30·64
Acetyl bromide	75·6°/751	1·6503	1·4511	20·06
Chloroacetyl chloride	105·0°/750	1·4202	1·4541	21·40
Trichloroacetyl chloride	116·4°/755	1·6179	1·4701	31·37
Phosphorus oxychloride	106·3°/758 (m. p. 1·4°)	1·6748	1·4606	25·11

The following data are available for comparison : Acetyl chloride, b. p. 50·9° (corr.) (Thorpe, J., 1880, **37**, 188); $D^{20°}_{4°}$ 1·1051; $n^{20°}_{D}$ 1·3898 (Brühl, *Annalen*, 1880, **203**, 11); $D^{20·6°}_{4°}$ 1·1039; $n^{20·8°}_{D}$ 1·388 (von Auwers and Schmidt, *Ber.*, 1913, **46**, 473). Propionyl chloride, b. p. 77·8—78·3°/724 mm.; $D^{20°}_{4°}$ 1·0646; $n^{20°}_{D}$ 1·4051 (Brühl, *loc. cit.*). *n*-Butyryl chloride, b. p. 101·4—102° (Reitter, *Z. physikal. Chem.*, 1901, **36**, 137); $D^{20°}_{4°}$ 1·0277; $n^{20°}_{D}$ 1·4121 (Brühl, *loc. cit.*). *n*-Valeryl chloride, b. p. 127—128°; $D^{15°}$ 1·0155 (Freundler, *Bull. Soc. chim.*, 1894, **11**, 312). *iso*Valeryl chloride, b. p. 113·5—114·5°/726 mm.; $D^{20°}_{4°}$ 0·9887; $n^{20°}_{D}$ 1·4155 (Brühl, *loc. cit.*). Acetyl bromide, b. p. 75·1°/746 mm.; $D^{15·8°}_{4°}$ 1·6625; $n^{15·8°}_{D}$ 1·4537 (Karvonen, *Ann. Acad. Sci. Fenn.*, 1914, *A*, **5**, 62). Chloroacetyl chloride, b. p. *ca.* 105°; $D^{0°}$ 1·495 (Wurtz, *Ann. Chim. Phys.*, 1857, **49**, 60). Trichloroacetyl chloride, b. p. 118° (corr.) (Gal, *Bull. Soc. chim.*, 1873, **20**, 12); $D^{16·2°}$ 1·6291, $D^{0°}_{4°}$ 1·6564 (Thorpe, *loc. cit.*). Phosphorus oxychloride, b. p. 105·8°/753 mm. (Walden, *Z. anorg. Chem.*, 1900, **25**, 212); m. p. 1·38 (Partington, " Text-Book of Inorganic Chemistry," 1926, p. 635); $D^{20°}_{4°}$ 1·675 (I.C.T.), $n^{25·1°}_{D}$ 1·460 (Zecchini, *Gazzetta*, 1893, **23**, 97).

Benzene. Kahlbaum's " thiophen-free " benzene, dried over sodium and carefully fractionated, was used as solvent. For calibration of the dielectric cell, Kahlbaum's " molecular-weight " benzene, which had been subjected to the same treatment, was used.

Carbon disulphide. Hopkin and Williams's A.R. liquid was shaken with mercury till no further blackening occurred, and dried over and then fractionated from phosphoric oxide. It was used immediately after purification.

Results.—The solvent is benzene, except where otherwise stated, and all the measurements are at 20°.

Acetyl chloride.

f_2.	$D^{20°}_{4°}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	0·8790	2·281	26·57	—
0·00976	0·8807	2·364	27·70	141·3
0·01989	0·8824	2·450	28·83	139·2
0·03040	0·8843	2·540	29·95	136·8
0·03950	0·8859	2·618	30·87	134·7

$P_{2\infty}$ = 143·5 c.c.; P_E = 16·8 c.c.; μ = 2·45.

Propionyl chloride.

f_2.	$D^{20°}_{4°}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	0·8784	2·276	26·52	—
0·01341	0·8807	2·403	28·31	160·0
0·02470	0·8825	2·507	29·71	155·8
0·03377	0·8841	2·590	30·78	152·8
0·04255	0·8855	2·671	31·79	150·4

$P_{2\infty}$ = 165·0 c.c.; P_E = 21·4 c.c.; μ = 2·61.

n-Butyryl chloride.

f_2.	$D^{20°}_{4°}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	0·8784	2·276	26·52	—
0·02021	0·8814	2·471	29·35	166·8
0·03112	0·8833	2·578	30·81	164·5
0·04281	0·8850	2·694	32·33	162·4
0·04914	0·8861	2·758	33·13	161·2

$P_{2\infty}$ = 170·5 c.c.; P_E = 26·0 c.c.; μ = 2·61.

n-Valeryl chloride.

f_2.	$D^{20°}_{4°}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	0·8792	2·280	26·55	—
0·00831	0·8804	2·359	27·77	173·1
0·01762	0·8816	2·448	29·09	170·7
0·02323	0·8824	2·501	29·86	169·2
0·03214	0·8837	2·586	31·08	167·4

$P_{2\infty}$ = 175·0 c.c.; P_E = 30·5 c.c.; μ = 2·61.

*iso*Valeryl chloride.

f_2.	$D^{20°}_{4°}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	0·8792	2·280	26·55	—
0·01490	0·8812	2·425	28·75	174·3
0·02910	0·8831	2·563	30·75	171·1
0·04119	0·8847	2·681	32·39	168·2
0·05590	0·8867	2·826	34·31	165·5

$P_{2\infty}$ = 177·5 c.c.; P_E = 30·6 c.c.; μ = 2·63.

Acetyl bromide.

f_2.	$D^{20°}_{4°}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	0·8784	2·276	26·52	—
0·01477	0·8880	2·405	28·27	145·1
0·02357	0·8941	2·486	29·31	145·1
0·03361	0·9001	2·580	30·49	144·8
0·03771	0·9030	2·620	30·97	144·6

$P_{2\infty}$ = 145·5 c.c.; P_E = 20·1 c.c.; μ = 2·43.

Chloroacetyl chloride.

f_2.	$D_{4°}^{20°}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	0·8792	2·278	26·53	—
0·00941	0·8833	2·343	27·44	125·3
0·01739	0·8870	2·400	28·22	125·2
0·02735	0·8916	2·474	29·20	125·5
0·03568	0·8956	2·535	29·97	124·9

$P_{2\infty} = 125{\cdot}5$ c.c.; $P_E = 21{\cdot}4$ c.c.; $\mu = 2{\cdot}22$.

Trichloroacetyl chloride.

f_2.	$D_{4°}^{20°}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	0·8790	2·280	26·56	—
0·00705	0·8854	2·293	26·80	61·2
0·01408	0·8919	2·306	27·04	60·6
0·02108	0·8983	2·319	27·28	60·8
0·02839	0·9050	2·333	27·53	60·7

$P_{2\infty} = 61{\cdot}5$ c.c.; $P_E = 31{\cdot}4$ c.c.; $\mu = 1{\cdot}19$.

Chloroacetyl chloride (in CS_2).

f_2.	$D_{4°}^{20°}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	1·2635	2·637	21·27	—
0·00683	1·2641	2·704	21·89	111·7
0·01380	1·2648	2·773	22·51	111·5
0·01939	1·2654	2·832	23·02	111·6
0·02545	1·2660	2·895	23·56	111·4

$P_{2\infty} = 111{\cdot}8$ c.c.; $P_E = 21{\cdot}4$ c.c.; $\mu = 2{\cdot}06$.

Phosphorus oxychloride.

f_2.	$D_{4°}^{20°}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	0·8784	2·276	26·52	—
0·01797	0·8930	2·427	28·65	145·4
0·02800	0·9012	2·512	29·81	144·2
0·03909	0·9102	2·611	31·09	143·4
0·04505	0·9150	2·662	31·73	142·3

$P_{2\infty} = 147{\cdot}5$ c.c.; $P_E = 25{\cdot}1$ c.c.; $\mu = 2{\cdot}40$.

SUMMARY.

The dipole moments of acetyl, propionyl, *n*-butyryl, *n*-valeryl, and *iso*valeryl chlorides have been measured, and it is shown that the moment increases in the series only as far as the second. An explanation for the large value of the moment of acetyl chloride has been suggested. The moments of acetyl bromide and iodide are compared with that of acetyl chloride. The moments of chloro- and trichloro-acetyl chloride can be explained on the assumption that the $\mathrm{C}{<}^{\mathrm{O}}_{\mathrm{Cl}}$ moment acts at an angle of 16° to the direction of the C—C axis. From the moment of phosphorus oxychloride a value for the $\mathrm{P} \longrightarrow \mathrm{O}$ moment is found.

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