

occurs. In hydrocarbons, two carbides may be formed— $Ta_6C_6$  and  $TaC$ . These both have very high melting points. The former has a specific resistance of about  $180 \times 10^{-6}$ , the latter of about  $18 \times 10^{-6}$ .

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

## ELECTRIC MOMENT AND MOLECULAR STRUCTURE. VII. THE CARBON VALENCE ANGLE

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The experimental examination of the angle between the valences of the carbon atom may seem an attempt to prove the obvious, but the calculations of Slater<sup>1</sup> and of Pauling<sup>2</sup> by means of wave mechanics that the angle is the regular tetrahedral valence angle,  $109.5^\circ$ , and the evidence as to the angle given by x-ray<sup>3</sup> and electron scattering<sup>4</sup> in gases make it desirable to extend the preliminary application of electric moments which has been made in the study of the problem.<sup>5</sup> This preliminary application was made in the case of the moments of the halogenated methanes. Rough kinetic theory diameters were calculated for chlorine, bromine and iodine by comparison with the dimensions of the corresponding inert gas structures and used as the internuclear distances of the halogens in the methylene halides. The assumption of these distances, when used with the carbon-halogen nuclear separations obtained by Pauling,<sup>6</sup> necessitated a widening of the angle between the C-X valences to  $124^\circ$  in methylene chloride,  $120^\circ$  in methylene bromide and  $135^\circ$  in methylene iodide. When the C-X dipole moments were resolved at these angles, the resultants agreed so well with the experimentally determined moments of the molecules that the moments were regarded as indicating these values for the angles between the C-X valences. However, it was stated that the disregard of the inductive effects of the dipoles as well as the speculative nature of the treatment of the atomic dimensions rendered the excellence of the agreement between the observed and the calculated values of the moments somewhat fortuitous. As the inductive action of each C-X dipole in the methylene halide lowers the moment of the other C-X dipole in the molecule, it is evident that the angle calculated between the dipoles without regard for this effect is too large, although it is interesting to note that the recent calculation by Bewilogua<sup>3</sup> from the results of x-ray scattering also

<sup>1</sup> Slater, *Phys. Rev.*, **37**, 481 (1931); *ibid.*, **38**, 1109 (1931).

<sup>2</sup> Pauling, *THIS JOURNAL*, **53**, 1367 (1931).

<sup>3</sup> Debye, *Z. Elektrochem.*, **36**, 612 (1930); Bewilogua, *Physik. Z.*, **32**, 265 (1931).

<sup>4</sup> Wierl, *Ann. Physik*, [5] **8**, 521 (1931).

<sup>5</sup> Smyth and Rogers, *THIS JOURNAL*, **52**, 2227 (1930).

<sup>6</sup> Pauling, *Z. Krist.*, **67**, 377 (1928).

gives  $124^\circ$  for the angle between the C-Cl valences in methylene chloride. As it appears impossible, at present, to calculate satisfactorily the lowering of the moments by induction, this complication has been avoided by removing the component dipoles so far from one another in the molecule as to render their mutual inductive effects negligible.

In the separation of the dipoles from one another advantage is taken of the fact that the valences directed outward from a benzene ring act in the plane of the ring so that para valences act in the same straight line in opposite directions.<sup>7</sup> Instead, therefore, of methylene compounds, para-substituted benzyl compounds as represented in Fig. 1 have been measured. In support of this procedure, not only the zero moments of *p*-dinitrobenzene, and *p*-dichloro-, *p*-dibromo- and *p*-diiodobenzene may be cited, but also the excellent agreement of the observed and calculated values when different groups are in the para positions. Thus, the electric moment of nitrobenzene is  $3.9 \times 10^{-18}$ <sup>8</sup> and that of chlorobenzene  $1.52 \times 10^{-18}$ . As the two dipoles should act in opposite directions in the same straight line in *p*-chloronitrobenzene, the resultant moment should be  $(3.9 - 1.52) \times 10^{-18} = 2.38 \times 10^{-18}$ , in excellent agreement with the observed value  $2.45 \times 10^{-18}$ . If the bromine moment  $1.50 \times 10^{-18}$  is substituted for the chlorine, the calculated value is  $2.40 \times 10^{-18}$  and the observed  $2.53 \times 10^{-18}$ . The results are a little less satisfactory in the case of the cyanides. As the moment of benzonitrile is indistinguishable from that of nitrobenzene, one would expect zero moment for *p*-nitrobenzonitrile, but the observed value is  $0.7 \times 10^{-18}$ . The moment of *p*-bromobenzonitrile should be  $(3.9 - 1.50) \times 10^{-18} = 2.4 \times 10^{-18}$ , while the observed value is  $2.64 \times 10^{-18}$ . For *m*-nitrobenzonitrile, in which the two dipoles should make an angle of  $120^\circ$  with each other, the moment should be  $3.9 \times 10^{-18}$ , and the observed value is  $3.8 \times 10^{-18}$ . As the agreement between the observed and calculated values for these two latter compounds is satisfactory and as the small moment apparently observed for *p*-nitrobenzonitrile may be due entirely to the effect of neglected atomic polarization, it seems justifiable to treat the moment

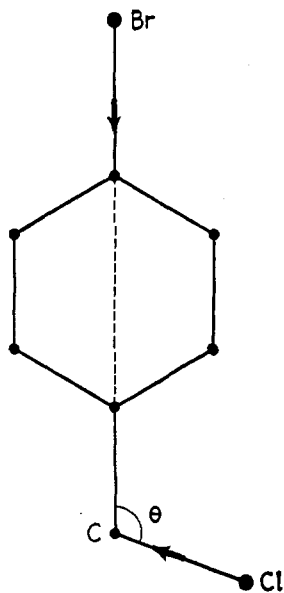


Fig. 1.—The *p*-bromobenzyl chloride molecule.

<sup>7</sup> Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Company, Inc., New York, 1931, Chap. VI.

<sup>8</sup> The values of moments, for which the experimental data are not given in this paper, are taken from the appendices of "Dielectric Constant and Molecular Structure."

associated with the cyanide group as acting in the direction of the line joining the group to the rest of the molecule. This implies that the carbon and nitrogen nuclei are in line with the nucleus of the carbon atom to which the group is attached, and is consistent with Pauling's conclusion that the HCN molecule is linear.<sup>2</sup>

A question may be raised as to the effect of the moments of the two principal dipoles upon each other. It has been shown that carbon-halogen dipoles exert an inductive effect, detectable in the observed moments, through only two carbon atoms of a saturated chain,<sup>5</sup> while the larger cyanide dipole has a measurable effect upon the third atom of the chain, but would affect the fifth to a hardly detectable extent.<sup>9</sup> Since, in the para-substituted benzyl compounds, the principal dipoles are separated by five carbon atoms it may be concluded that the moments of these dipoles would little affect one another. This is supported by the values of the moments of *p*-chloro- and *p*-nitrotoluene. As the moment of the toluene molecule,  $0.4 \times 10^{-18}$ , is regarded as acting in the direction of the line joining the methyl carbon to the ring with its positive end toward the former, the moment of *p*-chlorotoluene should be  $(0.4 + 1.52) \times 10^{-18} = 1.92 \times 10^{-18}$  and that of *p*-nitrotoluene should be  $(0.4 + 3.9) \times 10^{-18} = 4.3 \times 10^{-18}$ . As the two dipoles point in the same direction in each of the two molecules, the moment of each should be increased if there were any appreciable inductive action between them, but the observed moment of the one is  $1.74 \times 10^{-18}$  and of the other  $4.50 \times 10^{-18}$ , differing from the calculated values by no more than the possible error. It would thus appear that the moments of the two principal dipoles may be regarded as approximately independent of each other.

A final question may be raised as to whether it is justifiable to treat the moment of a molecule such as benzyl chloride as acting in the C-Cl line, *e. g.*, in the diagram of the *p*-bromobenzyl chloride molecule in Fig. 1, can the dipoles be represented merely by the two arrows shown, the effects of the C-H bonds and of the attachment of the -CH<sub>2</sub>Cl group to the ring being neglected? Unfortunately, we do not know the small moment, if any, associated with the C-H bond, for the arbitrary calculation of it by Eucken and Meyer<sup>10</sup> as  $0.4 \times 10^{-18}$ , though useful for some purposes, cannot be regarded as establishing its value. The moment of methyl chloride,  $1.86 \times 10^{-18}$ , must act in the line joining the carbon and chlorine nuclei. When one of the hydrogens is replaced by a methyl group to form ethyl chloride, the moment increases by  $0.15 \times 10^{-18}$  because of the moment induced in the added methyl group. It has been seen that, in toluene, a moment of  $0.4 \times 10^{-18}$  acts in the direction of the line joining the methyl carbon to the ring with its positive end toward the methyl carbon.

<sup>9</sup> Smyth, "Dielectric Constant and Molecular Structure," p. 99.

<sup>10</sup> Eucken and Meyer, *Physik. Z.*, **30**, 397 (1929).

In benzyl chloride a moment of about the same magnitude should occur in about the same location and should oppose the induced moment, as the induced dipole would have its positive end toward the ring. If the carbon valence angle is about  $110^\circ$ , the projection of what may be called the toluene moment,  $0.4 \times 10^{-18}$ , in the direction of the principal moment is  $0.14 \times 10^{-18}$ . In other words, the toluene moment is of such a size as to cancel approximately the increase in induced moment accompanying the replacement of a methyl hydrogen by a phenyl group, which is borne out by the agreement of the moment of benzyl chloride,  $1.85 \times 10^{-18}$ , with that of methyl chloride. The representation of the benzyl chloride moment by a single arrow in the C-Cl line appears, therefore, to be a justifiable approximation, and the similar representation of the moment produced by substitution of the bromine on the ring in Fig. 1 is certainly correct. Identical reasoning should apply to benzyl bromide and its substituted products, but uncertainty in the value for the moment of methyl bromide and the effect of atomic polarization upon the values for the higher alkyl bromides makes the reasoning inconclusive. However, the moment of benzyl bromide,  $1.86 \times 10^{-18}$ , is lower than that calculated for ethyl bromide without taking into account the atomic polarization by an amount identical with the difference between benzyl chloride and ethyl chloride. The moment of benzyl cyanide,  $3.52 \times 10^{-18}$ , is  $0.3 \times 10^{-18}$  higher than that of methyl cyanide, as might be expected from the greater inductive effect of the large cyanide dipole, which the toluene moment is not large enough to cancel. This small induced moment can, as an approximation, be treated as acting in the direction of the C-CN line and is, of course, included in the value  $3.52 \times 10^{-18}$  for the molecule. Evidently it is a justifiable approximation to treat the moment of a  $C_6H_5CH_2X$  molecule as acting in the C-X line and Fig. 1 may be regarded as an approximately correct representation of the moments. It is also evident that the larger the moments of the two principal dipoles, the smaller will be the relative effects of the approximations and neglected factors and the greater the accuracy of the value calculated for the valence angle  $\theta$ .

### Preparation of Materials

**Benzene.**—Merck's c. p. benzene was shaken with concentrated sulfuric acid until no coloration appeared, washed with water, with dilute sodium carbonate solution, and three times with water, dried over calcium chloride, twice fractionally crystallized, refluxed over phosphorus pentoxide and fractionally distilled, refluxed over sodium wire and distilled; b. p.  $80.2-80.3^\circ$  (757 mm.);  $n_D^{20}$  1.50135;  $n_D^{25}$  1.49815.

**Heptane.**—Material from the Ethyl Gasoline Corporation was fractionally distilled from phosphoric anhydride; b. p.  $98.2-98.3^\circ$  (757 mm.);  $n_D^{20}$  1.38775;  $n_D^{25}$  1.38530.

All the remaining materials were obtained from the Eastman Kodak Company.

**Benzyl Bromide.**—Material (b. p.  $80-83^\circ$ , 10 mm.) was fractionally distilled under reduced pressure, the fraction distilling at  $86.8-87.5^\circ$  (19 mm.) being collected. This fraction was redistilled; b. p.  $87.0-87.2^\circ$  (19 mm.);  $d_4^{25}$  1.4324.

**Benzyl Cyanide.**—Material (b. p. 98–100°, 8 mm.) was twice fractionally distilled under reduced pressure; b. p. 115.2–115.4° (19 mm.);  $n_D^{20}$  1.52327;  $n_D^{25}$  1.52086;  $d_4^{25}$  1.0119;  $d_4^{50}$  0.9914. A sample distilled from phosphoric anhydride had the same  $n_D^{20}$ .

***p*-Bromobenzyl Chloride.**—Material (m. p. 40–41°) was fractionally distilled under reduced pressure (b. p. 118–119°, 16 mm.), fractionally crystallized from petroleum ether, dried in a vacuum desiccator and twice fractionally crystallized; m. p. 41.3–41.5°.

***p*-Chlorobenzyl Bromide.**—Material (m. p. 48.5–49°) was twice fractionally crystallized from petroleum ether and dried in a vacuum desiccator; m. p. 48.5–48.7°.

***p*-Nitrobenzyl Bromide.**—Material (m. p. 98–99°) was twice fractionally crystallized from a mixture of dry benzene and petroleum ether, washed with petroleum ether and dried in a vacuum desiccator; m. p. 99.4–99.7°.

***p*-Nitrobenzyl Chloride.**—Material (m. p. 70–71°) was fractionally crystallized from carefully dried ether and dried in a vacuum desiccator; m. p. 71.2–71.5°.

***p*-Nitrobenzyl Cyanide.**—Material (m. p. 116°) was twice fractionally crystallized from dry benzene, washed with petroleum ether and dried in a vacuum desiccator; m. p. 116.6–116.8°.

### Experimental Results

The densities and dielectric constants of the solutions of the polar substances in the non-polar were measured with the apparatus and methods previously employed,<sup>11</sup> a wave length of 1000 meters being used in the dielectric constant determinations. In Table I the first column gives the mole fraction  $c_2$  of the polar substance in the heptane or benzene solution and the succeeding columns give the values at 25 and 50° of the dielectric constants  $\epsilon$  and the densities  $d$  of the solutions and the polarizations  $P_2$  of the polar substance.  $P_2$  is calculated by means of the usual equations

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2} \frac{c_1 M_1 + c_2 M_2}{d} \quad \text{and} \quad P_2 = \frac{P_{12} - P_1}{c_2} + P_1$$

in which  $P_{12}$  is the polarization of the mixture, and  $c_1$  and  $c_2$ ,  $M_1$  and  $M_2$  and  $P_1$  and  $P_2$  are, respectively, the mole fractions, molecular weights and polarizations of the individual components. The molar refraction for the D sodium line,  $MR_D$ , of benzyl bromide has been calculated from the atomic refractions given in Landolt-Börnstein (fifth edition), that of benzyl cyanide has been determined directly, and the values for the other substances have been calculated from measurements upon the solutions by means of equations analogous to those for  $P_{12}$  and  $P_2$ . These values have been used together with those for  $P_\infty$ , the polarization obtained by extrapolating the  $P_2$ - $c_2$  curve to infinite dilution, and the absolute temperature  $T$  to calculate the electric moment  $\mu$  by means of the equation

$$\mu = 0.0127 \times 10^{-18} \sqrt{(P_\infty - MR_D)T}$$

The absolute values of the moments are a little high because of the neglect of the atomic polarization  $P_A$ . The values of the molar refraction and of the orientation polarization  $P_\infty - MR_D$  and the moment calculated from the data at 25° and at 50° are listed in Table II, the solvent in which the compound was measured being given in the second column.

<sup>11</sup> Smyth and Walls, *THIS JOURNAL*, 53, 527 (1931).

TABLE I  
DIELECTRIC CONSTANTS, DENSITIES AND POLARIZATIONS

$\epsilon_2$	25°	50°	25°	50°	25°	50°
	$\epsilon$		$d$		$P_2$	
Benzene-Benzyl Bromide						
0.00000	2.276	2.226	0.8734	0.8465	(26.68	26.76 = $P_1$ )
.01085	2.332	2.275	.8817	.8546	108.7	104.2
.03019	2.427	2.360	.8957	.8682	106.8	102.6
.03526	2.453	2.383	.8998	.8723	106.4	102.2
.05612	2.555	2.475	.9150	.8875	104.9	100.9
.06180	2.582	2.499	.9190	.8915	104.4	100.5
.10706	2.801	2.696	.9513	.9236	101.6	98.2
Heptane-Benzyl Bromide						
0.00000	1.920	1.883	0.6795	0.6577	(34.58	35.62 = $P_1$ )
.03132	2.012	1.966	.6988	.6770	109.9	104.9
.04016	2.038	1.989	.7043	.6823	109.3	104.3
.05976	2.097	2.042	.7166	.6944	108.4	103.6
.07896	2.155	2.095	.7288	.7063	107.3	103.0
.12994	2.315	2.241	.7613	.7384	105.3	101.7
.18084	2.493	2.403	.7971	.7737	103.7	100.4
Benzene-Benzyl Cyanide						
0.00996	2.446	2.376	0.8751	0.8483	274.7	259.7
.01438	2.522	2.443	.8761	.8493	270.1	256.3
.02490	2.698	2.601	.8782	.8515	261.2	248.9
.03031	2.790	2.682	.8792	.8526	257.6	245.2
.03877	2.933	2.809	.8808	.8543	251.4	240.1
.04734	2.076	2.936	.8825	.8561	245.3	234.9
Heptane-Benzyl Cyanide						
0.00691	1.984	1.941	0.6814	0.6597	289.3	273.4
.01538	2.059	2.010	.6835	.6619	277.8	267.4
.01684	2.072	2.021	.6838	.6621	276.9	265.6
.01978	2.100	2.046	.6846	.6630	276.8	264.6
.02638	2.157	2.098	.6863	.6647	270.0	259.0
.02821	2.170	2.113	.6869	.6652	665.7	258.3
.03115	2.195	2.135	.6876	.6660	263.2	255.1
.04263	2.291	2.226	.6905	.6690	254.2	248.3
.04683	2.325	2.260	.6917	.6702	250.7	246.4
Heptane- <i>p</i> -Bromobenzyl Chloride						
0.02849	1.994	1.951	0.7031	0.6812	102.0	98.5
.04298	2.031	1.985	.7149	.6928	101.1	97.9
.05875	2.072	2.023	.7282	.7059	100.3	97.3
.08259	2.135	2.080	.7475	.7250	99.7	96.5
.09698	2.175	2.118	.7597	.7373	99.5	96.6
Heptane- <i>p</i> -Chlorobenzyl Bromide						
0.02134	1.975	1.934	0.6966	0.6746	103.5	100.7
.03418	2.008	1.964	.7070	.6849	102.5	99.3
.04634	2.039	1.993	.7168	.6945	101.7	98.9
.05775	2.069	2.020	.7260	.7036	101.3	98.3
.07166	2.106	2.054	.7372	.7147	101.0	98.1
.08658	2.146	2.091	.7492	.7267	100.7	97.8

TABLE I (Concluded)

$n_D$	25°	50°	25°	50°	25°	50°
$n_D$	$n_D$	$n_D$	$n_D$	$n_D$	$n_D$	$n_D$
Benzene- <i>p</i> -Nitrobenzyl Bromide						
0.00556	2.378	2.318	0.8798	0.8528	300.1	287.6
.00907	2.442	2.375	.8838	.8568	296.8	283.7
.00918	2.443	2.376	.8839	.8569	294.7	282.8
.01333	2.518	2.443	.8886	.8615	291.5	278.9
.01794	2.602	2.517	.8938	.8668	287.6	274.3
.02386	2.711	2.614	.9005	.8735	283.4	270.3
.03314	2.884	2.767	.9108	.8839	277.5	264.9
Benzene- <i>p</i> -Nitrobenzyl Chloride						
0.00741	2.413	2.347	0.8785	0.8516	299.3	281.9
.00880	2.438	2.369	.8795	.8525	297.2	280.2
.01551	2.560	2.477	.8840	.8570	289.8	274.4
.01556	2.561	2.476	.8840	.8570	290.2	273.6
.02530	2.737	2.633	.8904	.8639	281.2	265.9
.03035	2.829	2.714	.8936	.8671	277.1	262.7
.03555	2.926	2.799	.8971	.8706	273.7	259.7
.04185	3.042	2.903	.9013	.8749	269.2	256.2
Benzene- <i>p</i> -Nitrobenzyl Cyanide						
0.00303	2.342	2.287	0.8753	0.8483	346.8	340.3
.00546	2.394	2.334	.8767	.8498	343.6	332.7
.00714	2.430	2.366	.8777	.8508	340.4	329.3
.00736	2.434	2.370	.8778	.8509	339.2	328.4
.01059	2.506	2.433	.8798	.8529	339.3	325.2
.01420	2.587	2.503	.8819	.8551	337.3	320.5
.01555	2.617	2.528	.8827	.8559	336.0	318.1
0.00351	2.354	2.298	0.8755	0.8486	354.3	345.9
.00846	2.463	2.396	.8785	.8516	347.0	335.3
.01053	2.506	2.436	.8797	.8529	341.0	330.7
.01178	2.536	2.460	.8804	.8536	342.5	328.2
.01512	2.611	2.526	.8824	.8556	339.5	324.4

TABLE II

## REFRACTIONS, ORIENTATION POLARIZATIONS AND ELECTRIC MOMENTS

Compound	Solvent	$M_{RD}$	$P_{25^\circ} - M_{RD}^{50^\circ}$	$25^\circ$	$50^\circ$	
				$\mu \times 10^{16}$		
Benzyl bromide	Benzene	38.69 <sup>a</sup>	71.0	66.0	1.85	1.85
	Heptane		73.0	67.0	1.87	1.87
Benzyl cyanide	Benzene	35.22	250.8	232.8	3.47	3.48
	Heptane		262.8	243.8	3.55	3.56
<i>p</i> -Bromobenzyl chloride	Heptane	43.9	61.1	56.6	1.71	1.72
<i>p</i> -Chlorobenzyl bromide	Heptane	44.1	61.4	57.9	1.72	1.74
<i>p</i> -Nitrobenzyl bromide	Benzene	45.2	262.8	245.8	3.55	3.58
<i>p</i> -Nitrobenzyl chloride	Benzene	42.7	266.3	243.3	3.58	3.60
<i>p</i> -Nitrobenzyl cyanide	Benzene	40.8	307.2	300.2	3.84	3.95
			318.2	312.2	3.91	4.03

<sup>a</sup> Calculated value.

### Discussion and Interpretation of Results

The moment found for benzyl bromide in heptane is not experimentally distinguishable from that found in benzene solution. In the case of benzyl cyanide, the value found in heptane solution is slightly higher than that in benzene, but, as the low solubility of *p*-nitrobenzyl cyanide in heptane necessitates the use of benzene as solvent, the value for benzyl cyanide found in benzene is used in the calculation of the valence angle, although the mean value  $3.52 \times 10^{-18}$  may be taken for general use as the moment of the molecule. As the moment found for *p*-nitrobenzyl cyanide showed an increase with increase in temperature, a second set of measurements was made upon this substance, the results of which are listed in Tables I and II below those of the first set. The rise with temperature is observed in both sets of measurements, although the agreement is rather unsatisfactory because of the small concentrations of the polar substance necessitated by its low solubility. As no reason for this variation with temperature is apparent in the structure of the molecule,<sup>12</sup> it may possibly arise from incomplete elimination of the effect of intermolecular action by extrapolation of the  $P_2$ - $c_2$  curve. The considerable variation of  $P_2$  with concentration in the very dilute solutions shows the effect of the large dipoles upon one another's orientation, an effect which would be reduced by rising temperature. In view of these circumstances, a value slightly higher than the mean has been adopted for the moment.

The valence angle  $\theta$  of carbon has been calculated by means of the equation for the resultant  $\mu$  of two vectors,  $m_1$ , and  $m_2$ , which make an angle  $\theta$  with each other. The equation may conveniently be written in the form

$$\cos \theta = \frac{\mu^2 - m_1^2 - m_2^2}{2m_1m_2}$$

In Table III,  $\mu$  is the moment observed for the molecule of the para-substituted benzyl compound, the formula of which is given in the first column,  $m_1$  is the moment of the unsubstituted benzyl compound, that is, of the C-Cl dipole in Fig. 1, or of one similarly located, and  $m_2$  is the moment of the dipole in the para position. The values are taken from Table II or from the literature.<sup>8</sup>

TABLE III  
ELECTRIC MOMENTS ( $\times 10^{18}$ ) AND THE CARBON VALENCE ANGLE

	$\mu$	$m_1$	$m_2$	$\theta$
<i>p</i> -BrC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Cl	1.72	1.85	1.50	119°
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Br	1.73	1.86	1.52	119.5°
<i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Cl	3.59	1.85	3.9	113.5°
<i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Br	3.57	1.86	3.9	114°
<i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CN	4.00	3.48	3.9	114°

<sup>12</sup> Cf. Smyth, Dornte and Wilson, THIS JOURNAL, 53, 4242 (1931).



The values of the carbon valence angle calculated from the moments of the two para-halogen substituted compounds agree well with one another, as do those calculated from the three para-nitro substituted compounds. The intra-molecular dimensions are such that one would expect little, if any, widening of the valence angle by repulsion between the ring and the side chain. Any such repulsive effect should not be altered by the replacement of a halogen by a nitro group in the para position. It is reasonable to conclude, therefore, that the difference of  $5^\circ$  between the results calculated from the para-halogen substituted compounds and those from the para-nitro is due to the fact that, in the latter, the larger values of the moments render relatively smaller the effects of the approximations necessary in the treatment. As the  $4^\circ$  difference from the theoretical tetrahedral angle may easily arise from these approximations as well as from small errors in  $\mu$ ,  $m_1$  and  $m_2$ , it may be concluded that the carbon valence angle determined in these compounds agrees with the theoretical angle of  $109^\circ 28'$  within the limit of the error of experiment and calculation, although, in some cases, the angle may well depart from this value more or less. The results are in excellent agreement with Pauling's estimate of values of  $112$  and  $115^\circ$  from crystal structure data and with Wierl's calculation from electron scattering that the angle between the C-Cl valences in methylene chloride lies between  $110$  and  $115^\circ$ . The satisfactory outcome of this treatment establishes the validity of the method, which is now being applied to the determination of the oxygen and sulfur valence angles.

### Summary

The electric moments of several benzyl and para-substituted benzyl compounds have been determined and used together with values in the literature to calculate the angle between the valences of the carbon atom. The value obtained,  $114^\circ$ , differs from the theoretical tetrahedral angle by no more than the probable error.

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