with the absorption and slow combustion equipment than can be obtained without the diffusion apparatus.

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Dipole Moment and Group Rotation. I. The Moments of the Chloro- and Nitrobenzyl Chlorides and the Effect of Group Separation[1]

By J. M. A. de Bruyne, Rose M. Davis and Paul M. Gross

Discussion of the effect of rotation of component dipoles within molecules on their dipole moments has been confined largely to substituted straight chain hydrocarbons with two identical polar groups at each end. Ethylene chloride is the simplest case. By increasing the length of the hydrocarbon chain, it has been sought to separate the like polar groups at its ends and so study their interactions as a function of the distance separating them.[2]

Unless an extended zigzag chain is assumed with the polar groups rotating about its ends, the number of possible configurations such a molecule can assume by rotation about the various bonds is very great, so that conclusions concerning the interaction of the polar groups as affected by their separation must be drawn with considerable reservation.

The substituted benzyl halides are compounds in which this uncertainty is eliminated, since the benzene ring fixes the position of the second polar group and defines its separation from the rotating halide group in the side chain. This paper gives the results of the determination of the dipole moments of the ortho, meta, and para chlorobenzyl chlorides and the ortho and meta nitrobenzyl chlorides in different solvents. These are the first of a series of measurements designed to extend broadly the experimental background of this field by measuring the dipole moments of molecules containing varying types of rotating groups located at different distances apart in the molecule.

Method.—The dielectric constant ϵ, density d, and refractive index for the sodium D line n_D were determined for dilute solutions of these compounds at 30 ± 0.01°. The molar polarization P_2 of the solute at each concentration was calculated from the equation of Debye[3] in the form

$$P_2 = \frac{\epsilon - 1}{\epsilon + 2}\frac{M_2}{d}\frac{w_1 + w_2}{w_2} - \frac{w_1}{w_2}\frac{M_2}{M_1}P_1 \qquad (1)$$

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(1) Part of a thesis submitted by J. M. A. de Bruyne in partial fulfilment of the requirements for the Ph.D. degree in Chemistry at Duke University, in June, 1932.

(2) Compare Smyth and Walls, This Journal, **54**, 2261 (1932).

(3) Debye, "Polar Molecules," Chemical Catalog Co., New York, 1929, p. 45.

in which w_1 and w_2 are the weights, and M_1 and M_2 the molecular weights of the solvent and solute, respectively, and P_1 is the molar polarization of the solvent. The molar refraction R_2 of the solute was calculated by substituting for ϵ the square of the refractive index for the sodium D line in equation (1), and for P_1, the molar refraction of the solvent R_1 for the sodium D line. By plotting the values of P_2 against the mole fraction c_2 of the solute and extrapolating to $c_2 = 0$, the molar polarization of the solute P_∞ at infinite dilution was found. The dipole moment μ was then calculated from the equation

$$\mu = 0.0127 \times 10^{-18} \sqrt{(P_\infty - R_2)T} \text{ e. s. u.} \quad (2)$$

Apparatus.—The dielectric constants were determined by the heterodyne beat method employing an arrangement of apparatus similar to that of Williams and Weissberger[4] and others.[5]

A plate-tuned circuit was used in each oscillator so that the various condensers could be grounded, and the entire electrical system was carefully shielded. The beat note was matched with the 1000-cycle note of an electrically excited fork.

The standard condenser was a General Radio Company Precision Condenser, of 500 mmf. capacitance, with a scale of 2500 divisions, and was calibrated by a step method.[6]

Capacitance measurements were made at a frequency of 10^6 cycles/sec.

The measuring condenser was of brass, gold plated, and consisted of three concentric cylinders in an outer brass container. These were mounted by rods on a bakelite lid machined to fit the brass container which was at ground potential. The inner and outer cylinders were connected together. A switch was so arranged that it could connect the middle cylinder either to this pair or to the container, thus providing a minimum or maximum capacitance. The difference between the two values (approximately 100 mmf. air capacitance) measured in corrected scale readings of the standard condenser was used in calculating the dielectric constant. This type of measurement eliminated any uncertainty from lead corrections and also the errors due to changes in the frequency of the oscillators with time.

A correction was necessary for the capacitance of that part of the condenser above the liquid level and due mainly to the rods with the bakelite of the lid as dielectric between them. As this was constant, it was evaluated by obtaining the difference values of the condenser for the standards dry air and benzene. The correction k so found was approximately 6% of the difference value for air. The dielectric constant ϵ of a liquid was then calculated from the equation

$$\epsilon = (\Delta S + k\epsilon')/(\Delta S' + k) \quad (3)$$

in which ΔS and $\Delta S'$ represent the difference values in corrected scale readings for the liquid and for the standard, respectively, and ϵ' the dielectric constant of the standard.

Such difference measurements made on two portions of the standard condenser scale agreed within 1 part in 3000 in every case, and in most instances were within one part in 5000.

Materials

Benzene.—Kahlbaum best grade of benzene was dried over phosphorus pentoxide and fractionated in a Dufton still with a 1.8-m. column. The main fraction distilling within 0.01° range was fractionally crystallized until a fraction of maximum freezing temperature was obtained. Benzene freezing within 0.02° of this temperature was

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(4) Williams and Weissberger, THIS JOURNAL, **50**, 2332 (1928).

(5) Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Company, New York, 1931, p. 54.

(6) Compare Linton and Maass, THIS JOURNAL, **53**, 957 (1931).

used as the solvent. It was distilled from freshly cut sodium when needed: b. p. 80.05°; $n_D^{30°}$ 1.49486; d_4^{30} 0.86840 (average).

Heptane.—Heptane from the Ethyl Gasoline Corporation was shaken with concentrated sulfuric acid, sodium hydroxide, mercury and distilled water, then dried over calcium chloride, over phosphorus pentoxide, and then fractionated. The fraction used had the constants: b. p. 98.47–98.52°; n_D^{30} 1.38292; d_4^{30} 0.67520.

Carbon Tetrachloride.—Eastman best grade was fractionated twice, giving material with the constants: b. p. 76.74°; n_D^{30} 1.45454; d_4^{30} 1.5747.

o-Chlorobenzyl Chloride.—Four hundred and fifty grams from Eastman Kodak Company was repeatedly fractionated at reduced pressure in a Hickman still. Forty-five grams of liquid boiling between 109.0 and 109.2° at 25.6 mm. was obtained. A chlorine analysis of the compound was made by the method described by Vaughn and Nieuwland:[7] chlorine found, 44.02; calcd., 44.05.

m-Chlorobenzyl Chloride.—This was prepared by chlorinating *m*-chlorotoluene. The liquid after shaking with potassium carbonate solution and drying over potassium carbonate and calcium chloride, was fractionated at reduced pressure. The sample used boiled at 111.0–111.2° at 25.4 mm.

p-Chlorobenzyl Chloride.—A sample from Eastman Kodak Company was fractionally crystallized and distilled at reduced pressure. The best fraction obtained after repeated fractionation froze between 28.2–28.4°; b. p. 114.0° at 25 mm.

The total chlorine content was determined by Vaughn and Nieuwland's method: chlorine found, 43.82, 43.91; calcd., 44.05. Side chain chlorine was determined by hydrolysis with alcoholic potassium hydroxide and subsequent analysis of the aqueous solution for chlorine: chlorine found, 22.4; calcd., 22.0. Oxidation of a sample of the compound by refluxing with alkaline permanganate solution gave the anticipated *p*-chlorobenzoic acid. These tests, which seemed desirable because of the results reported by Bergmann and Engel[8] for this substance, conclusively established the identity and purity of our sample of *p*-chlorobenzyl chloride.

o-Nitrobenzyl Chloride.—A sample from the British Drug Houses, Ltd., was recrystallized first from ligroin and then fractionally crystallized. A sample with f. p. 48.0–48.25° was used.

m-Nitrobenzyl Chloride.—A sample similar to the ortho compound was obtained by the same method and had f. p. 45.15–45.35°.

Results

As a check on the apparatus and method the dipole moment of chlorobenzene was determined in benzene as solvent and was found to be $\mu = 1.56D$,[9] a value identical with that found by other recent workers.

The data for the concentrations, dielectric constants and refractive indices of the solutions of the compounds are given in Table I and the polarizations and dipole moments are summarized in Table II. Bergmann and Engel[8] have determined the moment of *p*-chlorobenzyl chloride and find $\mu = 2.11D$. This value is so different from that found here ($\mu = 1.71D$ in benzene) that we are led to conclude that Bergmann and Engel were either dealing with some other substance or that there was some un-

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[7] Vaughn and Nieuwland, *Ind. Eng. Chem., Anal. Ed.*, **3**, 274 (1931).

[8] Bergmann and Engel, *Z. physik. Chem.*, [B] **15**, 85 (1931).

[9] We will designate the values of the moments in terms of the Debye (D) as suggested in the "Physikalisch-chemisches Taschenbuch," S. Hirzel, Leipzig, 1932, Vol. I, p. 123, and accepted by others. (Compare Weissberger and Sängewald, *Z. physik. Chem.*, [B] **20**, 145 (1933).) $1D = 1 \times 10^{-18}$ e. s. u.

explained source of error in their measurements on this compound. Our values in the three different solvents agree well and are also practically the same as those for the similar compounds *p*-bromobenzyl chloride ($\mu = 1.71D$) and *p*-chlorobenzyl bromide ($\mu = 1.72D$) measured by Smyth and Walls,[10] as would be expected from the closeness of the values of the C–Cl and C–Br vector moments. The identity and purity of our sample seems well established as previously noted (see. p. 3938).[11] Moreover, a molecular weight determination in benzene solution by the freezing point method gave a value 158.8 as compared to the theoretical value 161.0.

Values for the dipole moments of the other substances have not been reported previously.

Discussion

An exact treatment of the observed moments of the compounds measured here by the method of group moments of Eucken and Meyer[12] should also take into account the moments induced in any one bond by all others following the procedure of Smallwood and Herzfeld.[13] Such an exact treatment has been applied to these compounds but to avoid duplication it will be reserved for presentation in a later paper along with the results of measurements of the moments of bromo and iodo substituted compounds of the benzyl halide type. The induction effects are more important in these cases because of the larger polarizabilities of the C–Br and C–I group moments.

In the present paper we will follow a procedure which gives a good approximation to this more rigorous treatment in the cases of the para and meta substituted benzyl chlorides. Its use is possible because calculation shows that as the —CH_2Cl group assumes various rotational positions, the moment induced in it and the moments induced by it are practically constant in value when the ring substituent is in either para or meta position.

The observed moment of benzyl chloride,[14] $\mu = 1.85D$, which is well established experimentally, may be regarded as representing the resultant of all the inherent bond moments and all the induced moments in the ring and side chain. Similarly the observed moment ($\mu = 1.56D$) of chlorobenzene is the resultant of all the inherent bond moments and the induced moments in the molecule. If the direction of the vector representing the benzyl chloride molecule were known, it would be possible to combine it vectorially with the observed vector for chlorobenzene and obtain the moment of *p*-chlorobenzyl chloride, because the slight difference in induction effects of the chlorine and —CH_2Cl groups, respectively, on the groups

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(10) Smyth and Walls, THIS JOURNAL, **54**, 1860 (1932).

(11) As this manuscript was being submitted for publication a determination of this moment in benzene appeared by Weissberger and Sängewald [*Z. physik. Chem.*, **B20**, 148 (1933)]. They find $\mu = 1.74D$, in excellent agreement with our value of $\mu = 1.71D$.

(12) Eucken and Meyer, *Physik. Z.*, **30**, 397 (1929).

(13) Smallwood and Herzfeld, THIS JOURNAL, **52**, 1919 (1930).

(14) Smyth, Ref. 5, p. 203.

para to them are negligible. By using the observed value $\mu = 1.70D$ for *p*-chlorobenzyl chloride together with those of chlorobenzene and benzyl chloride it is possible to calculate the direction of the benzyl chloride vector

TABLE I

c_2	d	ϵ	P_2	n_D	R_2
		o-Chlorobenzyl chloride–benzene			
0.0000	0.86836	2.2626		1.49486	
.0048221	.87108	2.3018	157.0	1.49543	42.3
.009941	.87398	2.3441	157.2	1.49587	41.5
.014905	.87670	2.3842	156.3	1.49628	41.4
.020187	.87960	2.4274	155.3	1.49670	41.3
.025262	.88240	2.4694	154.7	1.49739	41.7
		o-Chlorobenzyl chloride–carbon tetrachloride			
0.00000	1.57471	2.2149		1.45454	
.0029367	1.57361	2.2351	149.1	1.45494	41.0
.005783	1.57255	2.2550	149.6	1.45536	41.1
.0088668	1.57133	2.2764	149.4	1.45568	40.6
.011665	1.57020	2.2960	149.3	1.45604	40.8
.015042	1.56888	2.3195	148.9	1.45676	41.7
		o-Chlorobenzyl chloride–heptane			
0.0000	0.67519	1.9030		1.38292	
.002926	.67675	1.9147	144.5		
.006035	.67834	1.9273	145.2	1.38374	39.5
.009375	.68002	1.9415	147.7	1.38422	40.1
.012244	.68152	1.9528	146.1	1.38470	40.8
.018312	.68467	1.9786	146.8	1.38565	41.0
		m-Chlorobenzyl chloride–benzene			
0.0000	0.86843	2.2627		1.49490	
.004397	.87085	2.2890	126.3		
.008926	.87339	2.3165	126.4	1.49547	40.1
.01489	.87664	2.3511	124.7	1.49613	41.1
.02402	.88151	2.4045	123.7	1.49686	41.2
.03992	.89006	2.5004	123.1	1.49816	41.1
		m-Chlorobenzyl chloride–carbon tetrachloride			
0.0000	1.5747	2.2157		1.45454	
.004009	1.5731	2.2381	127.2	1.45501	39.3
.008102	1.5714	2.2601	126.4	1.45558	41.0
.01212	1.5698	2.2817	125.5	1.45616	41.2
.02011	1.5666	2.3253	124.9	1.45738	41.7
.03534	1.5607	2.4083	123.5	1.45959	41.5
		m-Chlorobenzyl chloride–heptane			
0.0000	0.67523	1.9025		1.38292	
.004147	.67729	1.9168	130.3	1.38332	37.9
.007952	.67936	1.9299	128.9	1.38398	39.6
.01200	.68141	1.9435	127.6	1.38453	40.0
.01977	.68533	1.9702	127.3	1.38574	40.9
.034619	.69298	2.0217	126.3	1.38836	42.0

TABLE I (*Concluded*)

c_2	d	ϵ	P_2	n_D	R_2
p-Chlorobenzyl chloride–benzene					
0.0000	0.86836	2.2627		1.49491	
.005037	.87115	2.2840	100.5	1.49536	40.8
.010272	.87399	2.3067	101.2	1.49577	41.3
.015503	.87683	2.3287	100.6	1.49603	40.7
.02064	.87956	2.3509	100.8	1.49647	40.8
.02586	.88238	2.3727	100.4	1.49695	41.1
p-Chlorobenzyl chloride–carbon tetrachloride					
0.0000	1.5746	2.2157		1.45454	
.003062	1.57345	2.2277	101.0	1.45483	38.8
.006025	1.57223	2.2394	101.8	1.45529	40.9
.008808	1.57115	2.2501	101.4	1.45564	40.7
.01246	1.56962	2.2653	101.6	1.45624	41.3
.01511	1.56858	2.2749	100.7	1.45663	41.5
p-Chlorobenzyl chloride–heptane					
0.0000	0.67522	1.9032		1.38292	
.005002	.67778	1.9154	99.2	1.38358	39.7
.009921	.68030	1.9275	100.0	1.38431	40.6
.01481	.68276	1.9393	99.7	1.38512	41.4
.01988	.68536	1.9521	100.0	1.38588	41.5
o-Nitrobenzyl chloride–benzene					
0.0000	0.86841	2.2627		1.49486	
.0009047	.86902	2.2840	385.4		
.002973	.87042	2.3323	379.9	1.49515	41.6
.004429	.87138	2.3665	378.0	1.49536	42.7
.006026	.87247	2.4037	374.7	1.49554	42.4
.007489	.87349	2.4383	372.8	1.49573	42.2
o-Nitrobenzyl chloride–carbon tetrachloride					
0.0000	1.57469	2.2157		1.45430	
.002474	1.57394	2.2638	354.1	1.45470	42.3
.003950	1.57349	2.2926	352.5	1.45503	43.9
.005491	1.57311	2.3234	352.5	1.45526	43.2
.006936	1.57270	2.3514	349.7	1.45560	43.9
m-Nitrobenzyl chloride–benzene					
0.0000	0.86842	2.2627		1.49491	
.001934	.86973	2.3024	339.6	1.49517	42.4
.002794	.87029	2.3197	337.0	1.49523	42.4
.005889	.87238	2.3829	333.1	1.49562	42.5
.008984	.87445	2.4459	329.0	1.49598	42.5
.01183	.87641	2.5055	327.3	1.49627	42.2
m-Nitrobenzyl chloride–carbon tetrachloride					
0.0000	1.57475	2.2157		1.45436	
.001515	1.57425	2.2445	348.7	1.45466	44.2
.003010	1.57378	2.2729	346.7	1.45486	43.0
.004437	1.57335	2.2992	341.8	1.45509	43.1
.005988	1.57298	2.3283	339.3	1.45539	42.9
.007438	1.57259	2.3558	337.2	1.45577	43.9

TABLE II

	Solvent	P_2^∞	$P_2^\infty - R_2$	$\mu \times 10^{18}$
o-Chlorobenzyl chloride	Benzene	158.0	116.5	2.39
	CCl_4	149.5	108.5	2.30
	Heptane	144.2	103.5	2.25
m-Chlorobenzyl chloride	Benzene	126.8	85.9	2.05
	CCl_4	127.1	85.8	2.05
	Heptane	129.8	89.1	2.09
p-Chlorobenzyl chloride	Benzene	100.9	60.0	1.71
	CCl_4	101.6	60.5	1.72
	Heptane	99.4	58.6	1.69
o-Nitrobenzyl chloride	Benzene	385.6	343.4	4.10
	CCl_4	355.6	312.4	3.91
m-Nitrobenzyl chloride	Benzene	341.4	299.0	3.82
	CCl_4	352.4	309.0	3.89

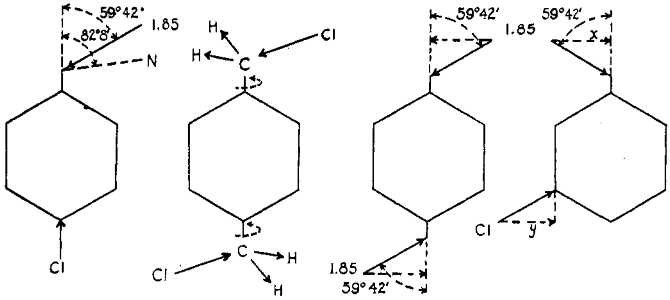
TABLE III

Compound	Av. obs. moment	Calcd. moment	Angle	Distances, Å. Min.	Max.
p-Xylylene dichloride	2.23	2.26	59°42′	6.34	6.50
m-Chlorobenzyl chloride	2.06	2.10	59°42′	4.36	4.95
m-Nitrobenzyl chloride	3.86	4.01	63°46′	4.36	4.95
o-Chlorobenzyl chloride	2.31	2.70	59°42′	2.38	3.33
o-Nitrobenzyl chloride	4.00	4.75	63°46′	2.38	3.33

whose magnitude is 1.85*D*. This is in effect an evaluation of the constant contribution that a —CH_2Cl group attached to a phenyl group will make to the observed moment of a compound of which it is a part. This contribution will be constant in compounds with ring substituents para or meta to the —CH_2Cl group provided the moments of such substituent groups are not so large as to induce moments of appreciable magnitude in the —CH_2Cl group. These induced moments will be proportional to the inverse cube of the distance and for the separations involved in the meta and para cases will be small and will not vary greatly with rotation.

Under these assumptions we have calculated the angle as 59°5′ that the vector 1.85 makes with the vertical axis of the ring as shown in Fig. 1(a). The moment of benzyl chloride as calculated from the group moments of Eucken and Meyer is 1.86*D*, disregarding induced effects, and makes an angle of 82°8′ as shown by the dotted line N of Fig. 1(a). The tilt upward by 22° to the angle 59°5′ is a measure of the induced moments in the molecule. It is to be emphasized that this tilting does not necessarily imply any distortion of the normal carbon valence angles but simply determines the direction of the resultant vector of the benzyl chloride molecule relative to the axis of the ring passing through the carbon linked to the —CH_2Cl group.

Since in the para compounds the separation between the dipole of the para group and that of the C–Cl bond of the —CH_2Cl group is constant and independent of rotation, then the angle for this vector calculated for different para substituted benzyl chlorides should remain substantially unchanged. Such is the case. Using the moments of *p*-bromobenzyl chloride ($\mu = 1.70D$) and *p*-nitrobenzyl chloride ($\mu = 3.58D$) and the group moments C–Br = $1.50D$ and C–NO_2 = $3.99D$,[15] values for this angle of 60°19′ and 63°46′, respectively, are found showing that the angle is altered but little by the nature and degree of polarity of the para substituent.



(a) (b) (c) (d)

Fig. 1.

This angle, having been shown to be constant, may be used to calculate the moments of compounds containing the rotating —CH_2Cl group of the type shown in Fig. 1(b and d) where the effective component group moments are resolved into their respective vertical vectors and the horizontal rotating vectors x and y. If the effective mean of the latter for all rotational positions can be evaluated, it can be combined with the net vertical component to give the resultant moment of the molecule. For the assumption that all rotational positions are equally probable the effective mean of the two horizontal components is found from

$$\mu_H = \sqrt{\frac{1}{\pi}\int_0^{\pi}(x^2 + y^2 + 2xy\cos\Theta)d\Theta} = \sqrt{x^2 + y^2} \tag{4}$$

where Θ is the angle between the two considered as rotating independently in the same plane.

In the case of the compound *p*-xylylene dichloride (Fig. 1b and c), the vertical components cancel and the moment can be found directly from equation (4), each horizontal component being equal to 1.85 sin 59°42′. This is the average angle found from the observed moments of *p*-chloro- and *p*-bromobenzyl chloride. The value so calculated is $\mu = 2.26D$, in excellent agreement with the observed value $\mu = 2.23D$.[16]

Calculations similar to these have been applied to those molecules measured here whose moments depend on rotation, the results of which are

(15) The average of recent values. See Smyth, Ref. 5, pp. 195 and 203. For the moments of the para compounds see Ref. 10.

(16) Weissberger and Sängewald, *Physik. Z.*, **30**, 792 (1929). A result similar to ours for the calculated moment is given by these authors (see Ref. 11).

given in Table III together with the angles employed. The agreement in the case of the meta chloro- and nitrobenzyl chlorides is good and may, if the validity of the approximate treatment used is granted, be taken as evidence that rotation in these compounds is practically free and unhindered. The large divergence in the case of the ortho compounds between calculated and observed values would on the same basis be attributed to hindrance of free rotation but is probably also due to the failure of the present treatment to weight correctly the induced effects in the ortho cases.

The relation of the separation of the principal dipoles to these results is seen from the last two columns of Table III. These give the maximum and minimum distances in Å. between these dipoles which are assumed to be located at the periphery of the carbon atoms concerned.[17] The table shows that there is practically free rotation when the principal dipoles do not approach each other closer than 4.4 Å. Even with approach of the dipoles to within about 3 Å. of each other in the ortho compounds there is a reduction of moment of only about 15% of that calculated for free rotation with the treatment used here. This small difference is of doubtful significance, however, since this approximate treatment would scarcely be valid for the ortho compounds as previously indicated.

The effect of the solvent on the observed moment and its relation to the freedom of rotation is seen from Table III. In *p*-chlorobenzyl chloride where every rotational position is equally probable, practically identical moments are found in the three solvents. The moments of the meta compounds which are close to those calculated here for free rotation differ but little in the different solvents, whereas fairly large differences are found for both ortho compounds, indicating that freedom of rotation in the case of small dipole separations is significantly affected by the solvent. No systematic regularity of effect of solvent is however apparent, indicating that other factors such as slight deviations from ideality may also cause part of the observed divergences. The indications are that the absence of divergences between values obtained in different solvents may be a valuable criterion for the existence of freedom of rotation.

Summary

The dielectric constants, densities and refractive indices of dilute benzene, carbon tetrachloride and heptane solutions of ortho, meta and para substituted benzyl chlorides have been determined at 30° and also those of dilute benzene and carbon tetrachloride solutions of ortho and meta nitrobenzyl chlorides. The dipole moments of these compounds have been discussed in relation to freedom of rotation as affected by the extent of separation of the groups concerned.

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[17] Based on the values of Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293 (1932).