

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Electric Moments of Phenylethylene and Substituted Phenylethylenes

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It has been shown by Otto and Wenzke¹ from a study of substituted phenyl acetylenes that phenylacetylene itself must have a moment of about 0.56 D and that the direction of this moment is opposite to that present in toluene. It will be of interest to obtain similar data on phenylethylene. Smyth and Dornte² conclude that phenylethylene has a zero moment. These authors also admit that their work does not necessarily rule out a moment somewhat smaller than 0.4 D. In order to correlate the moments of asymmetrical dichloropropylene, asymmetrical dichloroisobutylene and trichloroethylene, Bruyne Davis and Gross³ assumed a moment of 0.5 D for the group =C—H with the negative end of the moment toward the hydrogen end of the group.

Preparation of Compounds

Phenylethylene,⁴ *p*-methylphenylethylene,⁵ *p*-ethylphenylethylene,⁵ *p*-bromophenylethylene⁶ and *p*-chlorophenylethylene⁷ were prepared by the methods given in the references. *p*-Bromophenylethylene, after distillation with an efficient column at reduced pressure, was fractionally frozen. The mother liquor was removed by filtration, using a funnel which had a jacket filled with a mixture of ice and water. This process was repeated three times and then the compound melted at 5°. The other compounds were distilled at reduced pressure with an efficient column. In all cases the middle fraction, which contained one-half of the original material, was collected. The boiling points, density and refractive indices of these compounds are listed in Table I. As

these compounds are unstable after long standing, they were used within three hours of the final distillation. Samples of these compounds in solution in benzene showed no alteration in dielectric constant over this period of time.

Experimental Part

The apparatus used in the determination of dielectric constants has been described previously.⁸ Refractive indices were determined with a Pulfrich refractometer. The temperature of 25° was maintained by siphoning water from a constant temperature water-bath through the instrument. Oil from an electrically heated water-bath was used to obtain readings at 75°. The α and β lines of hydrogen and the D line of sodium were used for dispersion measurements.

Discussion of Results

It is difficult to determine with accuracy a small moment such as phenylethylene might be expected to have. The atomic polarization is such a large proportion of $P_A + M$ that considerable error would be made in neglecting it. In order to eliminate the uncertainty due to P_A it is necessary to obtain values of polarization at several temperatures. However, with a compound having a small moment the variation of the total polarization with temperature is small and this fact together with the error of extrapolating to zero concentration to obtain P_∞ makes it unsatisfactory to work with solutions. For these reasons it was decided to obtain data at various temperatures on the pure liquid. The assumption that the polarization of a pure unsymmetrical hydrocarbon liquid is the same as P_∞ is of course subject to some uncertainty. However, the variation of the total polarization of a pure liquid with temperature can be made to show definitely whether the compound has a moment. It will certainly be of interest to compare the moment obtained in this way from the pure liquid with that obtained by calculation from the more polar derivatives. Table III shows that there is a slight decrease in the total polarization of phenylethylene with an increase in temperature. This fact indicates that the compound

TABLE I

BOILING POINTS, DENSITIES AND REFRACTIVE INDICES OF COMPOUNDS

Compound	B. p., °C.	Mm.	d_{25}^{25}	n_{25}^{25D}
<i>p</i> -Bromophenylethylene	86-87	15		
<i>p</i> -Chlorophenylethylene	76-77	22	1.0449	1.55004
<i>p</i> -Methylphenylethylene	69-70	20	0.8813	1.52336
<i>p</i> -Ethylphenylethylene	84-85	19	.8901	1.52055
Phenylethylene	53-54	50	.8945	1.53423

(1) Otto and Wenzke, *THIS JOURNAL*, **56**, 1314 (1934).(2) Smyth and Dornte, *ibid.*, **53**, 1296 (1931).(3) Bruyne, Davis and Gross, *Physik. Z.*, **33**, 719 (1932).(4) "Organic Syntheses," **3**, 84 (1928).(5) Gauthier and Gauthier, *Bull. soc. chim.*, **53**, 323 (1933).(6) R. Quelet, *ibid.*, **45**, 75 (1929).(7) Sontag, *Ann. chim.*, **1**, 434 (1934).(8) Otto and Wenzke, *Ind. Eng. Chem., Anal. Ed.*, **5**, 187 (1934).

has a moment. The variation of the electronic polarization with temperature is sufficiently great that it will be necessary to determine it in order to calculate the change of P_M with temperature. The electronic polarization was calculated by extrapolating the values of the molecular refractivity to zero frequency assuming them a linear

TABLE II

MOLECULAR REFRACTIVITY AND REFRACTIVE INDEX OF PHENYLETHYLENE

Line	25°	75°	25°	75°
H α	35.942	36.295	1.53022	1.50433
Na β	36.175	36.535	1.53423	1.50829
H β	36.880	37.356	1.54677	1.52180
$\lambda = \infty$	35.23	35.52		

TABLE III

DIELECTRIC CONSTANTS AND DENSITIES OF SOLUTIONS OF SUBSTITUTED PHENYLETHYLENES (Solvent, benzene; temp. 25°)

c_2	d	ϵ	
<i>p</i> -Bromophenylethylene			
0.02352	0.8899	2.3439	
.03044	.8952	2.3670	
.04203	.9041	2.4032	
.06186	.9190	2.4608	
<i>p</i> -Chlorophenylethylene			
0.02122	0.8778	2.3293	
.03361	.8807	2.3622	
.05204	.8854	2.4110	
.07495	.8911	2.4712	
<i>p</i> -Ethylphenylethylene			
0.03569	0.87301	2.2971	
.05982	.87343	2.3122	
.08828	.87404	2.3279	
<i>p</i> -Methylphenylethylene			
0.08482	0.87250	2.3286	
.1068	.87268	2.3412	
.1604	.87311	2.3731	
Phenylethylene			
Temp., °C.	d	ϵ	P_2
25	0.8945	2.431	37.57
75	.8494	2.321	37.45

function of $1/\lambda^2$. Since the term $P_M T$ is constant, the equation $(P_M T)_{298} = (P_M T)_{348}$ can be used in solving for P_M at 298°K. By this method a moment of 0.37 D is obtained for phenylethylene.

The moments of *p*-bromophenylethylene, *p*-chlorophenylethylene, *p*-methylphenylethylene and *p*-ethylphenylethylene were determined by obtaining dielectric constant and density data on their solutions in benzene. The polarizations at infinite dilution were obtained by the method of Hedestrand.⁹ These moments are listed in Table IV. By taking the values of the moment of chlorobenzene, bromobenzene, toluene and ethylbenzene as 1.52, 1.50, 0.40, and 0.40, respectively, the moment of phenylethylene was calculated to be 0.17, 0.22, 0.23 and 0.21. The direction of this moment is opposite to that present in toluene and the same as that of phenylacetylene.

TABLE IV

POLARIZATION AND MOMENTS OF SUBSTITUTED PHENYLETHYLENES

Compound	P_∞	MR_D	$\mu 10^{18}$
<i>p</i> -Bromophenylethylene	88.13	45.16 ^a	1.35
<i>p</i> -Chlorophenylethylene	76.38	42.23	1.28
<i>p</i> -Methylphenylethylene	49.29	40.95	0.63
<i>p</i> -Ethylphenylethylene	53.31	45.15	.61
Phenylethylene			.37

^a Calculated from *p*-chlorophenylethylene.

Summary

1. The unsymmetrical structure of phenylethylene results in a moment of approximately 0.17–0.37 D.
2. The moment of phenylethylene is opposite in direction to that present in toluene.
3. Electric moments have been determined for *p*-bromo-, *p*-chloro-, *p*-methyl- and *p*-ethylphenylethylene and phenylethylene.

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(9) Hedestrand, *Z. physik. Chem.*, **B2**, 428 (1929).