These extrapolated values of P_∞ and the moments calculated by the relation $\mu = 0.0127 \times 10^{-18} \sqrt{(P - P_{\mathrm{M}})\,T}$ are listed in Table II. The moments obtained for methyl and ethyl benzoates are definitely higher than the values[15] (1.8 *D*) previously reported. The moments obtained for *d*-limonene and *d*-pinene are surprisingly high.

Summary

Measurements have been made of the dielectric constants and densities of solutions of *d*-pinene, *d*-limonene, methyl benzoate and ethyl benzoate in benzene to mole fractions as low as 0.0006. The sources of error in the experimental determinations were carefully examined and evaluated. From the data obtained, the dipole moments of the above substances were calculated by graphical extrapolation of the molar polarization to infinite dilution. The non-linearity of the curves relating ϵ_{12} to N_2 and d_{12} to N_2 for the more dilute solutions does not permit the use, in these cases, of Hedestrand's method of extrapolation and suggests that this method should not be considered of general applicability.

SCHENLEY PARK
PITTSBURGH, PA.

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[15] Estermann, *Z. physik. Chem.*, **B1**, 422 (1928).

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, COLLEGE OF ENGINEERING, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Directive Influence of the Electric Moment on Substitution in the Benzene Ring[1]

BY W. J. SVIRBELY AND J. C. WARNER

Latimer and Porter[2] predict whether a second group or atom will substitute in the meta or in the ortho and para positions to a group or atom already substituted in the benzene ring by estimating the polarity of the bond between the carbon atom of the ring and the "key" atom of the substituted group. The success of the Latimer–Porter rule made it seem logical to expect that a more satisfactory rule could be developed which would relate the directive influence to the electric moment of the mono substituted compound. Such a rule would have the advantage of being based upon a measurable property of the molecule which is determined by its structure. In Table I we have listed the mono substituted benzene derivatives whose moments have been determined. The compounds are divided into two groups depending upon whether the second substituted group is directed to the ortho and para or to the meta position. An examination of the data in Table I yields the interesting information that all compounds which direct substitution to the ortho and para positions have electric moments of 2.04 *D* or less while compounds which direct to the meta position have moments of 2.10 *D* or higher. This leads to the rule: *In general: if the electric moment of a mono substituted benzene derivative is greater than ∼ 2.07 D, the next substituted group will be directed to the meta position; if the moment is less than ∼ 2.07 D, the next group will be directed to the ortho and para positions.* Of the mono substituted benzene derivatives, whose moments had been determined, only three appeared as well-defined exceptions to the rule. These were benzoic acid, methyl benzoate and ethyl benzoate. It seemed entirely possible that the moments reported for these compounds were too low due to the fact that measurements of dielectric constants were not made in dilute enough solutions in non-polar solvents to eliminate all dipole interactions. The two esters have been reinvestigated in this Laboratory[3] with the result that moments decidedly higher than those previously reported were obtained. They are, therefore, no longer exceptions to the rule. This suggests that the moment of benzoic acid should be redetermined. It must be emphasized that factors such as the nature of the solvent, concentration, temperature, nature of reagent and the possibility of intermediate complex formation may cause a change in the effective electric moment of molecules and serve to cause exceptions to the simple rule based upon the electric moments of molecules in the gaseous state or in such dilute solution that all dipole interactions are absent. For example, according to the experiments of Hammick and Illingworth,[4] nitrosobenzene directs substitution

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[1] Abstracted from a part of the thesis submitted by W. J. Svirbely to the Committee on Graduate Instruction in partial fulfilment of the requirements for the degree of Doctor of Science.

[2] Latimer and Porter, THIS JOURNAL, **52**, 206 (1930).

[3] Svirbely, Ablard and Warner, *ibid.*, **57**, 652 (1935).

[4] Hammick and Illingworth, *J. Chem. Soc.*, **133**, 2358 (1930).

TABLE I

ELECTRIC MOMENTS AND THE OBSERVED ORIENTING INFLUENCE

Ortho-para substitution compound	$\mu \times 10^{18}$ e. s. u.	Meta substitution compound	$\mu \times 10^{18}$ e. s. u.
Phenyl-C_6H_5	0.0	Phenyl-CCl_3	2.10[a]
-$N{=}NC_6H$	.0	-$COOC_2H_5$	2.43[b]
-$CH_2CH_2C_6H_5$	.0	-$COOCH_3$	2.52[b]
-$CH{=}CHC_6H_5$	.0	-$CH_2COCH_2C_6H_5$	2.6
-CH_3	.4	-CHO	2.7
-C_3H_7	.4	-$COCH_3$	2.9
-C_4H_9	.4	-$COCH_2C_6H_5$	2.95
-C_5H_{11}	.4	-COC_2H_5	3.00[c]
-C_2H_5	.5	-NO	3.20
-$C{\equiv}CH$	.83	-$CHOHCOC_6H_5$	3.4
-OC_6H_5	1.0	-$COCOC_6H_5$	3.7
-OC_2H_5	1.0	-CN	3.91
-CH_2NH_2	1.1	-NO_2	4.08
-I	1.20		
-OCH_3	1.20		
-SCH_3	1.27		
-$CH_2SCH_2C_6H_5$	1.38		
-SH	1.4[c]		
-SC_6H_5	1.47		
-Br	1.50		
-F	1.50		
-Cl	1.52		
-NH_2	1.56		
-$N(CH_3)_2$	1.58		
-$NHCH_3$	1.64		
-CH_2OH	1.69		
-OH	1.70		
-CH_2OCOCH_3	1.80		
-CH_2Cl	1.85		
-CH_2Br	<1.85[c]		
-CH_2I	<1.85[c]		
-$CHCl_2$	2.04		

[a] Ortho and para in chlorination but meta in nitration.

[b] Values determined in this Laboratory which are decidedly higher than values previously reported.[3]

[c] Values which have been approximated from known values of similar compounds.

to the meta position, as predicted by the moment rule, in solvents in which it is not associated. In solvents in which it is associated and possesses a lower effective moment, however, it directs substitution to the ortho and para positions.

There are a number of mono substitution compounds which direct meta substitution, such as C_6H_5—NH_3X,—NR_3X,—$CONH_2$,—COCl,—SO_3H, —CH_2NO_2, whose moments have not been determined. There is, however, little doubt that all of these compounds would have moments greater than 2.07 *D*. Also, there are a number of mono substitution compounds which should be meta directing according to the moment rule: $C_6H_5N{=}C{=}O$, $\mu = 2.34\ D$; —$N{=}C{=}S$, $\mu = 2.76\ D$; —$N{\equiv}C$, $\mu = 3.49\ D$; —$C{\equiv}N{=}S$, $\mu = 3.59\ D$. The Latimer–Porter rule predicts that the first two would direct to meta and the last two would direct to ortho and para. Actually, since these unsaturated substances form addition rather than substitution compounds, they cannot be used to test the moment rule.

Summary

1. A study of the relation between electric moment and directive influence for substitutions in the benzene ring leads to the generally applicable empirical rule: If a mono substituted benzene derivative possesses an electric moment greater than ~ 2.07 *D*, a second group will be directed to the meta position; if the moment is less than ~ 2.07 *D*, the second group will be directed to the ortho and para positions.

2. The moment rule does not violate the principle of former polarity rules which were based upon a qualitative estimate of the polarity of bonds.

3. Since the effective moment of a molecule may vary with concentration, nature of solvent, temperature, nature of reagent and the formation of intermediate complexes, one may expect to find cases in which these factors make an important contribution to the directive influence.

SCHENLEY PARK
PITTSBURGH, PA.

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