

The New Orienting Rule of Svirbely and Warner.

THE new empirical rule in aromatic substitution, recently enunciated by Svirbely and Warner¹ as generally applicable, connecting the electric moment of the benzene derivative and the directive power, is open to many objections.

Claiming that there were only three definite exceptions to the rule, *i.e.*, the cases of benzoic acid, methyl and ethyl benzoates for which moments less than 2.07 D have been recorded,² the authors, apparently to justify their rule, have revised the moments of the last two compounds to 2.43 and 2.52 respectively and have advocated a redetermination in the case of benzoic acid. Without digressing about the validity of the experimental method adopted in their revision, we point out that Bergmann and Weirmann³ could, once more, only obtain the value of 1.91 for methylbenzoate and from what follows, it can be inferred that the rule is not based on grounds too solid to predict with certainty a moment greater than 2.07 D either for benzoic acid or for these esters.

Leaving aside the notorious case of the nitrosogroup, it is pointed out that benzoin,⁴ deoxybenzoin,⁵ and dibenzylketone,⁶ which have been classified by the authors as *meta* directing in accordance with their rule because of their moments 3.4, 2.95 and 2.65 respectively, have actually been found to have the opposite effect! The failure of

the rule in these cases is strictly in accordance with the expectation of the modern theories of aromatic substitution,⁷ and is not to be attributed to any of the factors referred to by the authors. It can also be predicted safely that the rule is bound to fail in the cases of the substituents like $-\text{CH}_2.\text{CH}_2.\text{CO}.\text{C}_6\text{H}_5$, $-\text{CH}_2.\text{SO}.\text{C}_6\text{H}_5$, $-\text{CH}_2.\text{SO}_2.\text{C}_6\text{H}_5$, $-\text{CH}_2.\text{SO}_2.\text{CH}_2.\text{C}_6\text{H}_5$, etc., all of which are expected to possess moments higher than 2.07 D but direct only to *ortho* and *para*.

Further, the following substituents have all been found to be *ortho* and *para* directing; but possess moments⁸ greater than 2.07 D: $\text{CH}:\text{CH}.\text{CHO}^9$ (3.71); $-\text{CH}_2.\text{CN}^{10}$ (3.56); $-\text{CH}:\text{CH}.\text{CO}.\text{CH}_3^{11}$ (3.3); $-\text{N}(\text{NO}).\text{C}_6\text{H}_5^{12}$ (3.39); $-\text{SCN}^{13}$ (3.00).

The dipole moment of the molecule can be claimed to bear a direct relation, as suggested in the rule, to the directive capacity of the substituent only if, according to the Robinson-Ingold theory of aromatic substitution, it decides the electronic disposition, as governed by the general polar and tautomeric effects, of the bond between the nuclear carbon and the attached atom of the substituent group. But this is not the case always¹⁴ particularly with complex substituent groups, where the rule has been shown to fail. If we consider the directive capacity of a *meta* directing group R with a high moment (*e.g.*, NO_2 , CN , $\text{SO}_2\text{R}'$) when attached to the ring through methylene groups (as in $-\text{CH}_2.\text{R}$, $-\text{CH}_2.\text{CH}_2.-\text{R}$), we find that even by the intervention of one carbon atom between R and the ring, the substituent becomes *ortho* and *para* directive, though the moment remains but little altered. Thus it is clear that this "measurable property of the molecule," the dipole moment, can be connected with the directive power only with strict limitations.¹⁵

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¹ *J. Am. Chem. Soc.*, 1935, **57**, 655.

² Table of Dipolemoments, *Trans. Farad. Soc.*, 1934, **30**, Appendix.

³ *J. Am. Chem. Soc.*, 1935, **57**, 1755.

⁴ Chattaway and Coulson, *J. Chem. Soc.*, 1928, 1081.

⁵ Pictet, *Ber.*, 1886, **19**, 1064; List, B., *ibid.*, 1893, **26**, 2452; Golubew, *ibid.*, 1878, **11**, 1939.

⁶ Manchot and Krische, *Ann.*, 1904, **337**, 176; Manchot and Zahn, *ibid.*, 1906, **345**, 331.

⁷ Waters, *Chem. Rev.*, 1930, **7**, 409, 420.

⁸ *Cf. ref. 2* for the moments recorded.