

# Proceedings of the Iowa Academy of Science

---

Volume 70 | Annual Issue

Article 39

---

1963

## Application of Guggenheim's Short Formula to the Calculation of Dipole Moments

Robert J. Buenker

George N. Schulte

Copyright © Copyright 1963 by the Iowa Academy of Science, Inc.

Follow this and additional works at: <https://scholarworks.uni.edu/pias>

---

### Recommended Citation

Buenker, Robert J. and Schulte, George N. (1963) "Application of Guggenheim's Short Formula to the Calculation of Dipole Moments," *Proceedings of the Iowa Academy of Science*: Vol. 70: No. 1 , Article 39.

Available at: <https://scholarworks.uni.edu/pias/vol70/iss1/39>

This Research is brought to you for free and open access by UNI ScholarWorks. It has been accepted for inclusion in Proceedings of the Iowa Academy of Science by an authorized editor of UNI ScholarWorks. For more information, please contact [scholarworks@uni.edu](mailto:scholarworks@uni.edu).

bathophenanthroline disulfonic acid. Filter the combined ethanol extracts through a coarse, fritted glass funnel. Pass the solution through a 3.5 x 40 cm.-column of cation exchange resin, IR-120, in the hydrogen form. Evaporate away the ethanol on a steam bath and take up the residue in 25 ml. of water. Neutralize the resulting solution with an approximately 1 N solution of iron-free, reagent grade sodium hydroxide, bringing the pH to 8.5, as measured with a pH meter. Evaporate this solution to dryness on a steam bath. Grind the residue in a mortar.

For bathophenanthroline: yield: 23.5 g, 97.5 per cent; equivalent weight found 268, 273, calculated for  $C_{24}H_{14}N_2(SO_3Na)_2$  268.2 (one-half the molecular weight). For bathocuproine: yield: 23 g., 97.5 per cent; equivalent weight found 278, 280, calculated for  $C_{26}H_{18}N_2(SO_3Na)_2$  282.2.

The infrared spectra of the sulfonated materials, are shown in the accompanying figures. The bands expected for the sulfonic groups (7) are present at  $9.65\mu$  and at  $8.40\mu$ . The spectra of the unsulfonated materials is found in the work of R. C. Smith (8).

#### Literature Cited

1. G. F. Smith, W. H. McCurdy, Jr., and H. Diehl. *Analyst*, 77, 418. 1952.
2. H. Diehl and G. F. Smith. The iron reagents: bathophenanthroline, 2,4,6-tripyridyl-s-triazine, phenyl-2-pyridyl ketoxime. G. Frederick Smith Chemical Company, Columbus, Ohio. 1960.
3. P. Trinder. *J. Clin. Pathol.* 9, 170. 1956.
4. D. Blair and H. Diehl. *Talanta* 7, 163. 1960.
5. G. F. Smith and D. H. Wilkins. *Anal. Chem.* 25, 510. 1953.
6. H. Diehl and G. F. Smith. The copper reagents; cuproine, neocuproine, bathocuproine. G. Frederick Smith Chemical Company. Columbus, Ohio. 1958.
7. L. J. Bellamy. *The infrared spectra of complex molecules.* J. Wiley and Sons, Inc. New York. Page 364. 1958.
8. R. C. Smith. 1961. Infrared spectra of substituted 1,10-phenanthrolines. Ph.D. thesis. Iowa State University Library. Pages 119 and 177.

## Application of Guggenheim's Short Formula to the Calculation of Dipole Moments<sup>1</sup>

ROBERT J. BUENKER and MSCR. GEORGE N. SCHULTE

*Abstract.* By substituting the actual physical constants of benzene into Guggenheim's short formula for orientation polarization, a simple relation for the dipole moment was obtained. The accuracy of this equation was tested with empirical data of some one hundred dipole moment measurements and the relation was found to agree within 0.02 debyes with calculations made using the Kumler-Halverstadt equations.

<sup>1</sup> The authors gratefully acknowledge the support of this work by the National Science Foundation during the past two years.

The dipole moment of a compound is most accurately determined by measuring the dielectric constant and density of the vapor at varying temperatures. However, when the compound is not sufficiently volatile for this procedure, dielectric constant, density, and refractive index measurements must be made for several dilute solutions of the substance in a non-polar solvent at constant temperature. Linear plots are then made of each of these physical properties against weight fraction of solute and these data are utilized in the Kumler-Halverstadt equations below to calculate the total polarization,  $P_T$ , and the molar refraction,  $R_M$ .

$$(1) P_T = \left[ \frac{\epsilon_1 - 1}{\epsilon_1 + 2} \cdot \frac{1}{d_1} \left( 1 - \frac{\beta_o}{d_1} \right) + \frac{3\alpha_o}{(\epsilon_1 + 2)^2 d_1} \right] M$$

$$(2) R_M = \left[ \frac{N_1^2 - 1}{N_1^2 + 2} \cdot \frac{1}{d_1} \left( 1 - \frac{\beta_o}{d_1} \right) + \frac{6N_1\gamma_o}{(N_1^2 + 2)^2 d_1} \right] M$$

In these equations,  $M$  is the molecular weight,  $\alpha_o$ ,  $\beta_o$ , and  $\gamma_o$  are the slopes of the linear plots of dielectric constant, density, and refractive index respectively;  $\epsilon_1$ ,  $d_1$ , and  $n_1$  are the corresponding intercepts ( $\omega = 0$ ).

The orientation polarization,  $P_o$ , is then taken to be equal to the difference between  $P_T$  and  $R_M$ . At 25°, the dipole moment,  $\mu$ , is equal to  $0.221\sqrt{P_o}$ .

It was noted by Guggenheim (1949), Smith (1950), and Palit (1952) that a convenient simplification of the formula for  $P_o$  could be made by assuming the Maxwell relation,  $\epsilon_1 = n_1^2$  (for benzene,  $\epsilon_1 = 2.2725$  and  $n_1^2 = 2.2416$ ). In particular it is seen that the left members of (1) and (2) become equal, and upon subtraction, are eliminated in the resulting equation for  $P_o$ . We then obtain two approximately equal equations for  $P_o$ , depending on whether we use  $\epsilon_1$  or  $n_1^2$ .

$$(3) \frac{M}{(\epsilon_1 + 2)^2 d_1} (3\alpha_o - 6N_1\gamma_o) \cong P_o \cong \frac{M}{(N_1^2 + 2)^2 d_1} (3\alpha_o - 6N_1\gamma_o)$$

The advantage of this procedure for Guggenheim was the elimination of  $\beta_o$ , which enables the calculation of  $P_o$  without the measurement of densities, since  $d_1$  depends on the solvent alone. Unfortunately, no such simplification can be made in the formula for molar refraction, and this quantity is valuable in the study of conjugated systems in particular.

The authors, therefore, undertook to utilize Guggenheim's short formula as a check on calculations involved in the Kumler-

Halverstadt equations. Since benzene is used exclusively in this lab as a solvent, the actual physical constants of this material were substituted for the intercepts in (3). In particular  $n_1 = 1.5$  was used for the coefficient of  $\gamma_0$ . Since  $\mu = 0.221\sqrt{P_0}$ , these simplifications enable us to write the following equation for the dipole moment:  $\mu = k\sqrt{M(\alpha_0 - 3\gamma_0)}$ . Now  $k$  can have either of two values.

$$(4) \quad K = \frac{0.383 d_1^{1/2}}{(\epsilon_1 + 2)} \quad , \quad K = \frac{0.383 d_1^{1/2}}{n_1^2 + 2}$$

Using  $\epsilon_1$ ,  $k = 0.09600$  and using  $n_1^2$ ,  $k = 0.09658$  (for benzene).

With these considerations in mind, a survey was made of the data for seventy-nine dipole moments measured at Loras in the past ten years. Especially, the expression,  $\sqrt{M(\alpha_0 - 3\gamma_0)}$  was computed for each of these measurements. The variance of the data was found to be quite small and the mean value was calculated to be 0.09625. It will be noted that the average of the two values of  $k$  obtained above is 0.09629.

Again using the data for the dipole moments measured in this lab,  $\mu_m$  was calculated according to the formula:

$$(5) \quad \mu_m = 0.09625 \sqrt{M(\alpha_0 - 3\gamma_0)}$$

In Table I below are listed  $\alpha_0$ ,  $\gamma_0$ ,  $\mu$ ,  $\mu_m$ , and the difference,  $\Delta\mu$ , between the last two quantities for ten of the above compounds (Dolter, 1956).

TABLE I  
Use of the Short Formula

Compound	$\alpha_0$	$\gamma_0$	$\mu$	$\mu_m$	$\Delta\mu$
<i>trans-p</i> -nitro- $\beta$ -cyanostyrene	0.8670	0.132	0.89	0.87	-0.02
<i>trans-p</i> -nitro- $\beta$ -bromostyrene	4.58	0.115	2.98	2.99	0.01
<i>trans-p</i> -bromo- $\beta$ -nitrostyrene	4.89	0.125	3.08	3.09	0.01
<i>trans-trans</i> -cinnamalacetone	8.36	0.156	3.54	3.55	0.01
<i>cis</i> -cinnamitrile	10.72	0.081	3.54	3.54	0.00
<i>trans-trans</i> -cinnamalacetaldehyde	10.21	0.0987	3.80	3.81	0.01
<i>trans</i> -cinnamitrile	14.51	0.096	4.12	4.13	0.01
<i>cis-p</i> -nitro- $\beta$ -cyanostyrene	15.21	0.091	4.90	4.91	0.01
<i>p</i> -dimethylamino- $\beta$ -methyl- $\beta$ -nitrostyrene	26.3	0.233	6.98	6.99	0.01
<i>trans-p</i> -dimethylamino- $\beta$ -nitrostyrene	33.1	0.243	7.58	7.59	0.01

The results showed that in all but five cases, the value obtained in this way varied at most with the previously computed dipole moment by 0.02 debyes. The exceptions can be grouped into two classes. Three of the measurements had determined intercepts in wide disagreement with the physical constants of benzene. Since the dielectric constant of benzene is assumed for the calibration of the dielectrometer, such variance cannot legitimately be attributed to anything other than experimental error. From a purely mathematical standpoint, failure to have intercepts approximately equal to the physical constants of the solvent violates the assumptions made in simplifying the original formulae.

In the second class were styrene and naphthalene, whose dipole moments were determined to be 0.18 D. and 0.00 D. respectively. The success of the formula (5) elsewhere is largely due to the negligibility of other factors in comparison with the dielectric slope,  $\alpha_0$ ; for such slightly polar substances as the two above,  $\alpha_s$  is not nearly so significant, and again the assumptions necessary to obtain (5) are not justified in this case.

To insure that these results were universally applicable, the dipole moments of twenty-eight compounds measured by Sutton (1951) were checked according to the above formula (5), and the error again was never more than 0.02 D.

We can then state that the formula for  $\mu_m$  (5) yields a value which differs from that obtained from the original formulae by not more than 0.02 D. if the following conditions are met: (1) the intercepts agree within 1% of the physical constants of the solvent; (2) the dipole moment is greater than 0.5 D.

In general the formula may be written,  $\mu_m = k\sqrt{M(\alpha_s - 2n_1\gamma_0)}$ , where  $k$  may be conveniently taken as the average of the two theoretical values given by (4). Alternately, using Palit's suggestion, we may take the geometric mean for  $k$ .

$$(6) \quad K = 0.383 [(\epsilon_s + 2)(n_1^2 + 2)d_1]^{-\frac{1}{2}}$$

#### Literature Cited

1. R. Dolter, et al., *Iowa Academy of Science Proceedings*, 63, 391-397 (1956).
2. K. B. Everard, L. Kumar, and L. E. Sutton, *J. Chem. Soc.*, 2811-2812 (1951).
3. E. Guggenheim, *Trans. Faraday Soc.*, 45, 714 (1949).
4. S. Palit, *J. Am. Chem. Soc.*, 74, 3952-3954 (1952).
5. J. Smith, *Trans. Faraday Soc.*, 46, 394 (1950).