[CONTRIBUTION FROM THE SPECTROSCOPY LABORATORY AND DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Quantitative Study of the Bonding of Chloroform-*d* in Various Solvents by Infrared Spectrometry[1]

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RECEIVED OCTOBER 19, 1954

Infrared studies have shown that the intensity of the carbon–deuterium stretching band in chloroform-*d* increases tenfold or more when the latter is mixed with certain solvents. This increase has been measured quantitatively for diethyl and di-*n*-butyl ethers, *p*-dioxane, anisole, acetone, acetic anhydride, ethyl acetate and pyridine. The association constant for the system diethyl ether–chloroform-*d* has been found to be 0.80 ± 0.15 l. mole^{-1} from the infrared data. A new method of preparation of chloroform-*d* is described.

Introduction

It is well known that mixtures of chloroform with oxygenated organic compounds show negative deviations from Raoult's law, this behavior being attributed to compound formation between the components. Further evidence indicating the same conclusion has been obtained from measurements of heats of mixing, viscosities, dielectric constants and freezing points. It is now generally accepted that the binding forces responsible for compound formation are due to hydrogen bonding. Some years ago Gordy[2] investigated this question by infrared spectroscopy. Because the C–H stretching band of chloroform overlaps with similar bands in the oxygenated solvents used by him, he confined his attention to the influence of chloroform on the spectrum of the solute. As the C–D stretching band of chloroform-*d* is free from such overlapping, it has seemed of interest to study the influence of a number of compounds, particularly diethyl ether, on the absorption of chloroform-*d* from a quantitative point of view.

The solution of certain polar organic compounds in chloroform or chloroform-*d* is accompanied by characteristic and drastic changes in the intensity of the C–H or C–D stretching absorption band. In some cases substantial frequency shifts are also observed. The main object of this work has been the quantitative determination of the intensity increase which takes place when chloroform-*d* is mixed with a number of compounds (see Table I).

TABLE I

INTENSITIES OF THE BONDED DEUTERIUM STRETCHING BAND OF CHLOROFORM-*d*

Compound	γ_C, l. cm.$^{-1}$ mole^{-1}	γ_C/γ_D[a]	$\nu - \nu_0$, cm.$^{-1}$	$\Delta\nu_{1/2}$, cm.$^{-1}$[b]
Diethyl ether	2.3	11.5	−10	16
Di-*n*-butyl ether	2.3	11.5	−11	15
p-Dioxane	3.6	18.0	− 5	14
Anisole	1.5	7.5	− 3	12
Acetone	2.5	12.5	0	11
Acetic anhydride	1.6	8.0	+ 7	21
Ethyl acetate	1.9	9.5	+ 3	13
Pyridine	4.1	20.5	−36	41

[a] All γ-values were measured in a 0.0225-mm. cell., γ_D = 0.20 l. cm.$^{-1}$ mole^{-1}. [b] $\Delta\nu_{1/2}$ is 10 cm.$^{-1}$ for pure $CDCl_3$.

Special attention has been paid to the system diethyl ether–chloroform-*d* with a view to determining the association constant. This particular system, which can be represented as

$$(C_2H_5)_2O + DCCl_3 \rightleftarrows (C_2H_5)_2O{\cdot}DCCl_3$$

gives rise to sharp absorption bands at 2253 and 2243 cm.$^{-1}$ (Fig. 1C) which are respectively associated with the free deuterium and bonded deuterium stretching vibrations.

Theoretical Part

The association constant, K, for a system of the above type is

$$K = \frac{c_C}{c_E c_D} \qquad (1)$$

where c_C is the equilibrium concentration in moles per liter of the complex (C), c_E that of ether (E), and c_D that of chloroform-*d* (D). To determine these concentrations, it was assumed that the Beer–Lambert law holds for all species present. D and C have a specific absorption near 2250 cm.$^{-1}$ (Fig. 1A-E), while E has very small continuous absorption which was corrected for by the procedure indicated below. The other systems listed in Table I also satisfy this requirement. Although no attempt has been made to determine their association constants, this could be done essentially as described below for the diethyl ether–chloroform-*d* system.

The quantity selected as a measure of absorption intensity is the apparent integrated intensity[3] B, which is given for any species i by

$$B_i = \frac{2.303}{c_i l} \int_{\text{band}} \log \frac{I_0}{I}\, d\nu \qquad (2)$$

where c_i is the concentration of the i species, l the thickness of the absorption cell, and I_0 and I the intensities of the incident and transmitted radiation, respectively, when the spectrometer is set at a frequency ν.

For the sake of simplicity, the following definitions are introduced

$$A_i = \int_{\text{band}} \log \frac{I_0}{I}\, d\nu$$

where A_i stands for the *area* of the absorption band associated with the species i, and

$$\frac{B_i l}{2.303} = \gamma_i = \text{constant}^{4}$$

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(1) The authors wish to acknowledge the support of the Office of Ordnance Research (Contract DA-19-020-ORD-896, Project TB5-0002 (5)), under whose auspices the present work was carried out. Heavy water was obtained by allocation from the AEC, whose coöperation is gratefully acknowledged.

(2) W. Gordy, THIS JOURNAL, **60**, 605 (1938).

(3) According to R. N. Jones, *et al.*, who studied the intensities of carbonyl bands of steroids (THIS JOURNAL, **74**, 80 (1952)), B is not different from the true integrated intensity for these compounds by more than about 2%. It is assumed that in the present work the difference is of the same order.

(4) A single cell has been used throughout this work so that l can be incorporated into γ_i.

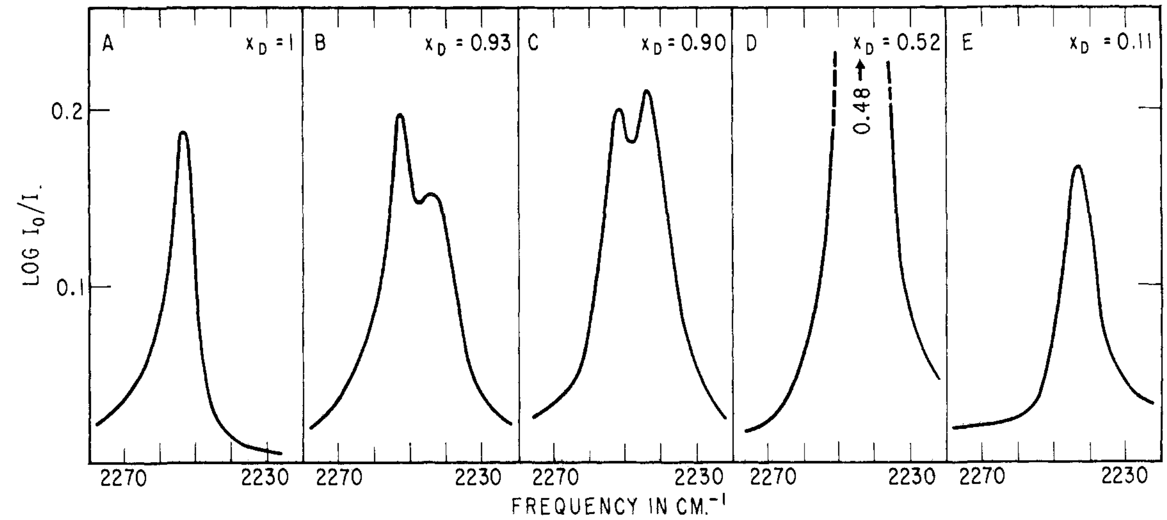

Fig. 1.—CD-stretching band in ether solution of chloroform-*d* at various mole fractions x_D.

Equation 2 now takes the simplified form

$$A_i = c_i\gamma_i \qquad (3)$$

The following relationships can then be written for the three species involved in the system under investigation and considered separately

$$A_D = c_D\gamma_D \qquad (4a)$$

$$A_E = c_E\gamma_E \qquad (4b)$$

$$A_C = c_C\gamma_C \qquad (4c)$$

Equation 4a gives γ_D directly from the spectrum of pure chloroform-*d*, for c_D is known and A_D is readily obtained from the absorption curve (Fig. 1A). A_E of eq. 4b is assumed zero as far as the 2250 cm.$^{-1}$ region is concerned since E has no specific absorption in this region; the justification of this assumption is based on the experimental procedures by which I_0 and I are measured. Equation 4c cannot be used directly to determine γ_C because the complex C exists only in solution and in equilibrium with D, which contributes to the absorption in the spectral region of interest.

It can be shown with the help of Beer's law that the total area A_m of the absorption bands associated with D and C for any equilibrium mixture is

$$A_m = \Sigma A_i = c_D\gamma_D + c_C\gamma_C \qquad (5)$$

If one prepares mixtures from known quantities of D and E and allows equilibrium to be reached, the initial concentrations of D and E, c°_D and c°_E, are related to the equilibrium concentrations in the following way[5]

$$c_D = c^\circ_D - c_C \qquad (6)$$

and

$$c_E = c^\circ_E - c_C \qquad (7)$$

Equations 5 and 6 can be combined to give

$$A_m = c^\circ_D\gamma_D + (\gamma_C - \gamma_D)c_C \qquad (8)$$

If the sum $c_D + c^\circ_E$ is denoted by c^0, the mole fraction of chloroform-*d* by x_D and the molar volumes of diethyl ether and chloroform-*d* by $\tilde{V}_E$ and $\tilde{V}_D$, respectively, then equations 1 and 8 lead to

$$A_m/c^\circ = \gamma_D x_D + {}^1/_2(\gamma_C - \gamma_D)[z - \{z^2 - 4x_D(1 - x_D)\}^{1/2}] \qquad (9)$$

where $z = 1 + (\tilde{V}_E - x_D\{\tilde{V}_E - \tilde{V}_D\})/K$. A plot of A_m/c^0 as a function of x_D produces the sort of curve shown by the solid line in Fig. 2. If eq. 9 is differentiated, and the slopes at $x_D = 0$ and $x_D = 1$ determined, these are found to be, respectively, $\gamma_D + (\gamma_C - \gamma_D)K/K + \tilde{V}_E$ and $\gamma_D + (\gamma_D - \gamma_C)K/K + \tilde{V}_D$. When K is large compared to $\tilde{V}_E$ and $\tilde{V}_D$, these two expressions reduce to γ_C and $2\gamma_D - \gamma_C$, respectively. Under these circumstances, since γ_D can be directly measured, γ_C can be determined from the limiting slope at either $x_D = 0$ or $x_D = 1$, that is, from dilute solutions of chloroform in ether or the reverse. If γ_C is large compared with γ_D, as in the present case, there is no particular reason for choosing one over the other.

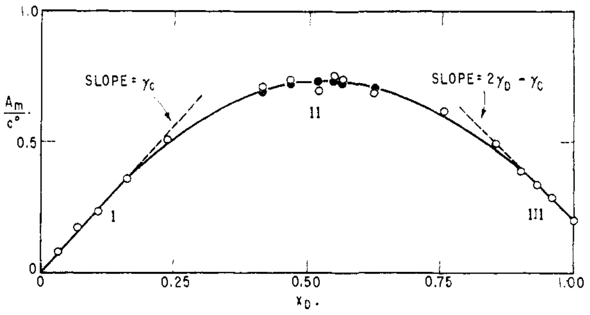

Fig. 2.—Integrated absorption intensity of the bonded CD-stretching band per unit concentration (A_m/c^0) *vs.* mole fraction x_D.

When γ_C and γ_D have been found, equations 5, 6 and 7 can be solved for the equilibrium concentrations and K may then be calculated from equation 1. This is the procedure that has been followed here. If the accuracy of the data justifies more rigorous treatment, equation 9 can be solved numerically for γ_C and K by substitution of the values of A_m/c^0 at suitably chosen pairs of values of x_D.

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[5] It has been shown by D. B. MacLeod and F. J. Wilson (*Trans. Faraday Soc.*, **31**, 596 (1935)) that the volume contraction on mixing equimolal amounts of diethyl ether and chloroform is 1.25%. Since this is rather small compared to our experimental error, it has been neglected throughout, but if necessary eq. 9 can easily be altered to include the effect.

Experimental Part

Preparation of Chloroform-*d*.—Earing and Cloke[6] prepared chloroform-*d* by treating calcium trichloroacetate with a solution of sodium deuteroxide in heavy water. In their procedure, the preparation of the anhydrous calcium salt is time-consuming and the use of sodium is inconvenient. Therefore a new method of preparation has been used in which calcium trichloroacetate is formed *in situ* from trichloroacetyl chloride and calcium carbonate in the presence of heavy water and at the same time cleaved to chloroform-*d* by the action of sodium carbonate. A mixture of dry calcium carbonate (15 g.) and sodium carbonate (16 g.)[7] is placed in a 0.5-liter, three-necked flask fitted with two small dropping funnels and attached to an apparatus similar to that described by Earing and Cloke[6] except for the bulb, which is replaced by a Friedrich condenser. The system is dried in the usual way. While the flask is immersed in a bath at 110°, heavy water (28 g., 99.5 atom % deuterium) is added and followed by the dropwise addition of trichloroacetyl chloride (48 g.). Chloroform-*d* is soon formed and distils over. The temperature of the bath is gradually raised to about 160° as required by the rate of distillation of the desired product. After two or three hours the reaction is over and the deuterated chloroform is removed (26 g., 81% yield based on the acid chloride). The temperature is raised and slight vacuum is applied to recover unreacted heavy water (23 g.). After drying and distillation, pure chloroform is obtained in 76% yield; $n^{25}\text{D}$ 1.4428. The isotopic purity has been determined by infrared spectrometry, the 1205 cm.$^{-1}$ band of normal chloroform being used as a working basis; the deuterium content has been found to be at least 98%.

Absorption Measurements.—Mixtures of diethyl ether and chloroform-*d* were prepared by weighing quantities of the components so that the volume of the solution was about 0.5 ml. The concentration range extended from 0 to 1 mole fraction of chloroform-*d*. Each solution was made up just before it was measured. The absorption data were obtained with a modified Perkin-Elmer Model 12B spectrometer described previously[8] and equipped with a lithium fluoride prism, and were recorded on a Brown strip-chart recorder. A spectral slit width of about 2 cm.$^{-1}$ was used. The spectrometer was flushed with dry nitrogen to reduce the absorption of carbon dioxide around 2350 cm.$^{-1}$ to a negligible percentage. The absorption cell consisted of two sodium chloride plates separated by a lead spacer and was provided with gasketed stoppers to prevent evaporation. It had a thickness of 0.0225 mm. as determined by the interference fringe method.[8] Radiation curves were determined before and after running each mixture, the cell being filled with a solution of diethyl ether in *normal* chloroform. This solution was so adjusted volumetrically that its concentration was close to that of the chloroform mixture to be measured. Since the refractive indices of chloroform-*d* and chloroform do not differ significantly, the radiation curve for each chloroform-*d* spectrum was thus measured on a sample of about the same refraction. From the absorption traces, the absorption curves were measured and plotted as log I_0/I *versus* the frequency in cm.$^{-1}$ (Fig. 1). The band areas A_m were then measured, the integration limits being so selected as to extend 40 cm.$^{-1}$ on both sides of the 2253 and 2243 cm.$^{-1}$ bands, *i.e.*, from 2293 to 2203 cm.$^{-1}$. No wing correction was applied as the measurement of band areas to 40 cm.$^{-1}$ on both sides of the band centers probably would not require a correction of more than 10%,[9] and the ratio of γ_C to γ_D was more significant than absolute intensities.

Results

From the area A_D under the band of chloroform-*d* (Fig. 1A) and equation 4a, a value of 0.20 l. cm.$^{-1}$ mole^{-1} was obtained[10] for γ_D. Band areas A_m were measured for sixteen diethyl ether–chloroform-*d* mixtures, three of which are shown in Fig. 1B-E. A plot of A_m/c^0 *versus* mole fraction of chloroform-*d* is given in Fig. 2. The slopes of the lines in regions I and III of this curve are γ_C and $(2\gamma_D - \gamma_C)$, respectively, yielding values of 2.2 and 2.4 l. cm.$^{-1}$ mole^{-1} for γ_C. For further calculations, the average value of 2.3 was used. From γ_C and γ_D it is possible to calculate the equilibrium concentrations and hence the association constant K, whose value is 0.80 ± 0.15 l. mole^{-1}. For this purpose, experimental values of A_m for mixtures of the concentration range $0.4 < x_D < 0.7$ (region II of Fig. 2) were used, since the relative error is least in this range. Experimental values of A_m/c^0, plotted as open circles in Fig. 2, are scattered to the extent of about 10%. The average value of K was used to calculate best values of A_m/c^0 and smooth the curve (full circles). From these results the ratio γ_C/γ_D is 11.5.

The above results indicate that within experimental error, γ_C can be determined from either side of Fig. 2. For the other systems listed in Table I, it was chosen to work with dilute solutions of the oxygenated compound in chloroform-*d*, *i.e.*, in region III. In Table 1, $\nu - \nu_0$ is the difference between the frequency ν of the bonded deuterium stretching band and that of the free deuterium band ν_0, which occurs at 2253 cm.$^{-1}$. $\Delta\nu_{1/2}$ is the half band width of the deuterium band for mixtures containing about 0.9 mole fraction of chloroform-*d*.

As pointed out previously, the C–H stretching band of normal chloroform, which occurs at 3020 cm.$^{-1}$, cannot be studied as described above because it is usually overlapped by the absorption of the solute. However, an oxygenated solute in which the hydrogen atoms have been replaced by deuterium is suitable. Acetone-d_6 was used and the following data were obtained: $\gamma_H = 0.59$, $\gamma_C = 5.91$, $\gamma_C/\gamma_H = 10.0$. $\Delta\nu_{1/2}$ is 18 cm.$^{-1}$ for free $CHCl_3$ and 21 cm.$^{-1}$ for bonded $CHCl_3$. Within experimental error, which is estimated to be 0.5 cm.$^{-1}$ or less, the complex absorbs at the same frequency as chloroform, which is also true for the acetone–chloroform-*d* system.

Discussion

As pointed out previously, either dilute solutions of chloroform-*d* in diethyl ether or dilute solutions of diethyl ether in chloroform-*d* can be used to determine γ_C. This indicates that the absorption of the complex is practically the same in both solvents. γ_C is proportional to the integrated absorption intensity of the C–D stretching band of the complex and γ_D, to that of chloroform-*d*, the proportionality factor being the same in both cases. Therefore the ratio γ_C/γ_D is a measure of the absorption of the former relative to that of the latter. This is, however, different from the ratio A_C/A_D which can be estimated as indicated below. A_C, being not measurable directly, can be calculated from equation 4c if the volume molality c_C of the pure complex is known. For the diethyl ether–chloroform-*d* system, on the assumption that the change of volume on mixing is negligible, c_C is equal to 5.72 moles per liter. Consequently, A_C is equal to 13.2 cm.$^{-1}$ and, since A_D is 2.45 cm.$^{-1}$, the ratio A_C/A_D is 5.4.

The value of K determined experimentally was used in connection with the law of mass action to

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[6] M. S. Earing and J. B. Cloke, THIS JOURNAL, **73**, 769 (1951).

[7] When sodium carbonate is used alone, the yield is about 60%.

[8] R. C. Lord, R. S. McDonald and F. A. Miller, *J. Opt. Soc. Am.*, **42**, 149 (1952).

[9] D. A. Ramsay, THIS JOURNAL, **74**, 72 (1952).

[10] c_D is equal to 12.46 moles per liter.

estimate the proportion of chloroform-*d* molecules which are bonded in an equimolar mixture of chloroform-*d* and diethyl ether at room temperature. The value obtained is 60%. This is somewhat higher than the figure of 45% calculated from vapor pressure data reported in the literature.[11]

The intensities of all the bands of symmetry species A_1 of chloroform and those of chloroform-*d* are related[12] to their frequencies in the following way

$$\sum \left(\frac{\gamma_i}{\nu_i^2}\right)_{\mathrm{H}} = \sum \left(\frac{\gamma_i}{\nu_i^2}\right)_{\mathrm{D}} \qquad (13)$$

Of the three vibrations belonging to species A_1 in chloroform, only ν_1, *i.e.*, the C–H stretching mode, is expected to be largely changed on deuteration. Therefore to a certain approximation, one can write

$$\frac{(\gamma_1)_{\mathrm{H}}}{(\gamma_1)_{\mathrm{D}}} \cong \frac{(\nu_1^2)_{\mathrm{H}}}{(\nu_1^2)_{\mathrm{D}}} \qquad (14)$$

The right-hand ratio in equation 14 is calculated as 1.80 from the frequency values. The ratio $(\gamma_1)_{\mathrm{H}}/(\gamma_1)_{\mathrm{D}}$ calculated from the observed values of $(\nu_1)_{\mathrm{H}}$ and $(\nu_1)_{\mathrm{D}}$ is 2.94. The difference shows that eq. 14 is not valid, *i.e.*, that vibration ν_1 is interacting to a considerable extent with ν_2 and ν_3 of the A_1 species in either chloroform-*d* or chloroform or both.

Acknowledgment.—The authors wish to thank Drs. C. M. Higgins and G. C. Pimentel, University of California, for an advance copy of their paper "Infrared Intensity of the C–D Stretch of Chloroform-*d* in Various Solvents." The only solvent studied both by these authors and by us is acetone. The absolute values of the apparent integrated absorption intensity *B* for acetone in their paper is not comparable with ours because of considerable differences in effective slit widths and temperature (32.5° *vs.* 22°). The ratio corresponding to γ_C/γ_D is calculated from their results to be 8.7, whereas we find 12.5. Part of this difference may be ascribed to temperature. Also the influence of carbon dioxide absorption on their readings may be significant. The authors would like to thank Professor George Scatchard for helpful discussion and suggestions.

CAMBRIDGE, MASS.

[11] A. A. Noyes and M. S. Sherrill, "A Course of Study in Chemical Principles," 2nd edition, The Macmillan Co., New York, N. Y., 1938, p. 260.

[12] B. L. Crawford, Jr., *J. Chem. Phys.*, **20**, 977 (1952).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Rotatory Dispersion of Some Metal–Amine Complexes

BY T. D. O'BRIEN AND R. C. TOOLE

RECEIVED AUGUST 16, 1954

The rotatory dispersion curves of several diamines were compared and found to have a common intercept corresponding to an optically active absorption band at 1380 Å. Active propylenediamine complexes with zinc, cadmium, silver and platinum show a constant dispersion ratio when the ratio of base to metal ion is less than 2. A different but constant ratio is obtained when the ratio is greater than 2. Other amines show similar behavior. This indicates the dispersive power is independent of the nature of the central metal atom and independent of the nature of the active diamines, but is dependent on the formation function $\bar{n}$. The dispersion ratio for a complex, optically active because of an active ligand, is quite different from the dispersion ratio of a resolved active metal complex, indicating that the source of optical activity differs in the two.

When an optically active base coördinates with a metal ion, the optical rotation of the resulting complex is sometimes opposite in sign to that of the active base and always different from the rotation due to the base alone. These changes in rotation have been explained by some as a partial induced asymmetry in the complex ion itself, and by others as a change in the contribution of the optically active ligand by the coördination.

It has been shown previously[1] that the optical rotation due to *levo*-propylenediamine[2] in a complex is dependent on the formation function $\bar{n}$. This present work was undertaken to see whether dispersive power, as distinct from the sign and magnitude of rotation, changes with complex formation, and is also dependent on the formation function $\bar{n}$. The quantity $\bar{n}$, first defined by Bjerrum,[3] is the average number of ligands bound per metal ion. The value of $\bar{n}$ may be readily determined by $\bar{n} = (C_c - C_l)/C_m$ where C_m = total concentration of all metal species, C_c = total concentration of ligand species present, and C_l = concentration of free or uncomplexed ligand.

The variation of rotatory power with wave length is most simply expressed by the Drude relation $\alpha = k/\lambda^2 - \lambda_0^2$ where α is the observed rotation at wave length λ, k is a constant, and λ_0 is the wave length corresponding to a characteristic frequency of vibration coupled to an optically active center. In general, however, the total rotation of a molecule is the sum of several partial terms of this type, so

$$[M] = \Sigma\, k_i/(\lambda^2 - \lambda_i^2)$$

In order to exhibit optical activity, the absorption bands at λ_1, λ_2, etc., must be optically active. For most colorless compounds these bands lie in the far ultraviolet, and the rotation in the visible increases gradually with decreasing wave length. While a change in solvent or temperature may often cause a change in the magnitude or even the sign of rotation, the dispersion ratio is usually unaffected. As used here the term dispersion ratio means simply the ratio of the optical rotations of a substance at two different wave lengths or $\alpha\lambda_1/\alpha\lambda_2$.

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[1] T. D. O'Brien and R. C. Toole, THIS JOURNAL, **76**, 6009 (1954).

[2] The following abbreviations are used, en = ethylenediamine, *l* = levo, *d* = dextro, *m* = *meso*, pn = propylenediamine, ptn = 2,4-diamino-*n*-pentane, tapn = 1,2,3-triaminopropane, chxn = 1,2-diaminocyclohexane, cptdin = 1,2-diaminocyclopentane, phenen = phenylethylenediamine, stien = stilbenediamine and buten = isobutylenediamine.

[3] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.