made for incorrect centering of the specimen and for absorption in the powder rod.[6]

The density of cesium chlorogermanate as determined pycnometrically was 3.45. From this figure and the value of a_0 the number of molecules in the unit cell was calculated to be 3.96. The number of molecules in the unit cell is therefore four, and the density calculated from X-ray data is 3.48.

The values for the intensities of the powder lines were calculated from the formula

$$I = \text{constant}\left(\frac{1 + \cos^2 2\theta}{\sin 2\theta \sin\theta}\right) jS^2 \text{ where}$$

$$S = f_{\text{Ge}} + 2f_{\text{Cs}} \cos 2\pi\left(\frac{h+k+l}{4}\right) + 2f_{\text{Cl}}(\cos 2\pi hx + \cos 2\pi kx + \cos 2\pi lx)$$

The atomic f-values of Pauling and Sherman[7] were used throughout these calculations. In order to determine the chlorine parameter, values of 0.22, 0.23 and 0.24 were used to calculate the intensities for the first ten lines. The value x = 0.23 gave the best agreement with the observed and was therefore used in the calculation of the remaining intensities. The observed intensities were corrected for absorption in the powder rod in the usual manner. The values for the observed and calculated intensities are given in Table II. The agreement is reasonable.

From the chlorine parameter of 0.23, the germanium–chlorine distance was calculated to be 2.35 Å. This is in good agreement with the value 2.34 Å. calculated from the ionic radii of Pauling.[2]

The authors wish to acknowledge the assistance of Professor J. L. Hoard who made available X-ray equipment and helped with the interpretation of the X-ray data.

Summary

1. The formation of chlorogermanic acid and its salts has been studied under a variety of conditions.

2. Evidence for the formation of negatively charged complex ions, presumably $GeCl_6^=$, when germanium tetrachloride is dissolved in concentrated hydrochloric acid has been obtained by migration experiments.

3. Cesium hexachlorogermanate has been prepared and its properties and crystal structure have been studied. It has a face-centered cubic lattice.

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[6] "Internationale Tabellen zur Bestimmung von Krystallstrukturen," Gebrüder Borntraeger, Berlin, 1935, pp. 581–582.

[7] Pauling and Sherman, *Z. Krist.*, **81**, 1 (1932).

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The Dielectric Constants of Some Pairs of Diastereomers

BY SAUL WINSTEIN AND REUBEN E. WOOD

Pairs of diastereomeric substances show no very characteristic differences in physical properties such as boiling point, polarizability, etc.[1] However, owing to the lack of free rotation about carbon–carbon single bonds[2] there is the possibility that the dipole moments and thus the dielectric constants of *meso* and *dl* compounds or *erythro* and *threo* compounds may differ sufficiently to be useful analytically. Also, there is the possibility that there may be enough regularity in these differences to allow the formulation of rules for the assignment of configuration to diastereomers on the basis of dielectric constant measurements. To study these possibilities and in some cases to obtain data immediately useful in analysis and identification we have determined the dielectric constants of some pairs of diastereomers available to us.

Materials

***meso*- and *dl*-2,3-Diacetoxybutanes.**—The *meso* isomer, m. p. 2.5°, b. p. (13 mm.) 83.6°, was prepared[3] from *meso*-2,3-butanediol, m. p. 34.0°, and distilled through a 40-cm. Weston column.[4] The *dl* isomer, m. p. 42.1°, was prepared[3] from the *dl*-2,3-butanediol from pure *cis*-2,3-epoxybutane.[5]

***dl*-*erythro*- and *dl*-*threo*-2,3-Diacetoxypentanes.**—These materials were kindly furnished us by Professor H. J. Lucas and Mr. M. J. Schlatter of these Laboratories.

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[1] Hückel, "Theoretische Grundlagen der organischen Chemie," Vol. II, Akademische Verlagsgesellschaft m. b. H., Leipzig, 1935, p. 125.

[2] See Weissberger, *J. Org. Chem.*, **2**, 245 (1937), for a review of configuration about single bonds.

[3] Wilson and Lucas, THIS JOURNAL, **58**, 2396 (1936).

[4] Weston, *Ind. Eng. Chem., Anal. Ed.*, **5**, 179 (1933).

[5] Winstein and Lucas, THIS JOURNAL, **61**, 1576 (1939).

Distillation through the Weston column yielded constant boiling materials; *erythro* isomer, b. p. (12 mm.) 90.4°; *threo* isomer, b. p. (12 mm.) 94.3°.

***dl-erythro-* and *dl-threo*-3,4-Diacetoxyheptanes.**—These materials were generously loaned us by Dr. W. G. Young of the University of California at Los Angeles. The *threo* isomer was pure while the *erythro* material needed redistillation. Distillation through the Weston column yielded constant boiling material, b. p. 114.2° (10 mm.).

***meso-* and *dl*-2,3-Dibromobutanes.**—These compounds were obtained as constant boiling materials from *meso*-2,3-diacetoxybutane and *trans*-2,3-epoxybutane[5,6] or the bromohydrin or 2-acetoxy-3-bromobutane derived from it. k_2 for the reaction of these dibromides with potassium iodide[7] in 99.00% methanol at 74.93° using synthetic methanol was 0.0553 for the *meso* preparation and 0.0298 for the *dl* compound.

***dl-erythro-* and *dl-threo*-2,3-Dibromopentanes.**—Very pure materials were generously made available by Mr. M. J. Schlatter.

***meso-* and *dl*-3,4-Dibromohexanes.**—These compounds were kindly supplied by Dr. W. G. Young.

***dl-erythro-* and *dl-threo*-2-Acetoxy-3-bromobutanes.**—These compounds were prepared as previously described[5,6] starting with pure *cis-* and *trans*-2,3-epoxybutanes.

Apparatus and Method

The dielectric constant measuring apparatus has been referred to in another paper.[8] As mentioned there the cell used was of the type described by Doborzynski.[9] For a cell of this type there may be derived an expression which relates approximately the cell's capacitance to the dielectric constant of the filling fluid. This will be of the form

$$\epsilon = \frac{l(C - m)}{1 - n(C - m)}$$

in which ϵ is the dielectric constant of the fluid, C the capacitance of the cell and l, m and n are constants characteristic of the cell. Such an equation was used to calculate the dielectric constants here reported. The values of l, m and n for the cell used were determined from measurements with fluids of known dielectric constant, *viz.*, air and the carefully purified liquids carbon tetrachloride, benzene, chlorobenzene, ethyl bromide, and ethylene dichloride. It was found possible to select values for l, m and n so that when the resulting equation was used to calculate the dielectric constants of the standard fluids ϵ's resulted which were on the average within 0.2% of the literature values we chose, namely, 1.001,[10a] 2.227,[10b] 2.272,[10c] 5.612,[10c] 9.21,[10d] 10.36.[10c]

Data and Discussion

Table I summarizes the dielectric constants, ϵ, we have obtained for the substances investigated. In the case of the *dl*-2,3-diacetoxybutane and *meso*-3,4-dibromohexane the values recorded are those obtained by linear extrapolation from the value for a mixture and the value for one pure diastereomer. These values are thus not as accurate as the others.

The values, in general, are listed to four significant figures to show the differences between the isomeric samples. The differences between the dielectric constant of the members of a pair of diastereomers are accurate enough to require so many figures even though the accuracy of the absolute values is only about 0.2%.

From a practical standpoint it is interesting to notice in Table I the very appreciable differences that exist in most cases between the dielectric constants of the isomeric substances. The dielectric constant is thus an excellent property for identification and even analysis in these cases that are usually otherwise quite difficult. An identification or analysis on the basis of a dielectric constant measurement is especially accurate if one or both of the pure isomers are available so that high accuracy for the absolute value of the dielectric constant is not necessary. Already the dielectric constants of the 2,3-dibromobutanes[5,6] and the 2,3-dibromopentanes[11] have proved very useful in these Laboratories.

TABLE I

PROPERTIES OF SOME PAIRS OF DIASTEREOMERS

Substance	Isomer	d^{25}_4	n^{25}_D	ϵ at 25°
2,3-Diacetoxybutane	*meso*	1.0213	1.4121	6.644
	dl	1.0235[a]	1.4133[a]	5.10[a]
2,3-Diacetoxypentane	*dl-erythro*	1.0022	1.4147	6.734
	dl-threo	1.0073	1.4175	5.228
3,4-Diacetoxyheptane	*dl-erythro*	0.9758 (20°)	1.4207	6.684
	dl-threo	0.9829 (20°)	1.4241	5.029
2,3-Dibromobutane	*meso*	1.7747	1.5091	6.245
	dl	1.7836	1.5125	5.758
2,3-Dibromopentane	*dl-erythro*	1.6724	1.5062	5.430
	dl-threo	1.6745	1.5064	6.507
3,4-Dibromohexane	*meso*	1.5940	1.5049	4.67[b]
	dl	1.5896	1.5031	6.732
2-Acetoxy-3-bromobutane	*dl-erythro*	1.3327	1.4489	7.268
	dl-threo	1.3320	1.4490	7.414

[a] Obtained by linear extrapolation using the values for one pure isomer and for a mixture of *meso* and *dl* isomers. Mixtures were measured either due to lack of material or to be able to perform the measurement at 25°. Mixture of 58.5% *dl* and 41.5% *meso* exhibited dielectric constant of 5.740. [b] See *a*. Mixture of 60.7% *dl* and 39.3% *meso* exhibited a dielectric constant of 5.922.

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(6) Winstein and Lucas, THIS JOURNAL, **61**, 1581 (1939).

(7) Dillon, Young and Lucas, *ibid.*, **52**, 1953 (1930).

(8) Wood and Dickinson, *ibid.*, **61**, 3259 (1939).

(9) D. Doborzynski, *Z. Physik*, **66**, 657 (1930).

(10) (a) "Int. Crit. Tab.," Vol. 6, p. 77; (b) Davies, *Phil. Mag.*, **21**, 1 (1936); (c) Sugden, *J. Chem. Soc.*, 768 (1933); (d) Smyth and Morgan, THIS JOURNAL, **50**, 1553 (1928);

(11) Lucas and Schlatter, unpublished work.

Dielectric constants have been reported previously for several of the compounds we have investigated. Sherrill and co-workers[12] have reported the dielectric constant of 2,3-dibromopentane prepared from 2-pentene obtained presumably by Boord's[13] synthesis as 5.43. This agrees with our value for *dl-erythro*-2,3-dibromopentane and indicates that the 2-pentene was pure *trans*-2-pentene. It is very interesting that the Boord synthesis gives essentially pure *trans*-2-pentene.

The 2,3-dibromobutanes have been previously investigated by Trieschmann,[14] but the materials employed by him were of doubtful purity. The dielectric constants 8.96 for the *meso* isomer and 8.72 for the *dl* compound reported by Trieschmann are about 50% larger than the values reported in this paper. In view of the values for the dielectric constants generally reported for substances of the type of the dibromobutanes it seems very unlikely that the dibromobutanes have dielectric constants as high as 8.96 and 8.72 and the finding of Trieschmann that *meso*- and *dl*-2,3-dibromobutane possess the same dipole moment possibly is incorrect also.

We had hoped that in a series of pairs of compounds such as the 2,3-diacetoxybutanes, 2,3-dibromobutanes, and 2-acetoxy-3-bromobutanes, there would be a regularity in the relative dielectric constants of the isomers. However, values obtained do not indicate a simple correspondence between relative dielectric constant and configuration. Since the *meso* isomer displays the higher dielectric constant in the case of both the dibromobutanes and the diacetoxybutanes, one might expect the *erythro*-2-acetoxy-3-bromobutane to exhibit a larger dielectric constant than the *threo* compound. Instead the last two compounds have nearly the same dielectric constant and that of the *threo* isomer is slightly larger.

In the case of the dibromobutanes, dibromopentanes, and dibromohexanes the situation is similar. The order of relative dielectric constants in the case of the dibromobutanes is different from the order obtaining for the other two pairs of dibromides. The greatest regularity observed was in the diacetoxyalkane series. For each of the three pairs of these compounds examined the *meso* or *erythro* isomer has the larger dielectric constant. In fact, the dielectric constants are nearly the same for corresponding members of the three different pairs of isomers.

Several expressions[15,16,17] relating the dielectric constant of liquids to the dipole moments of their molecules have been proposed. Using Onsager's equation

$$\mu^2 = \frac{(n^2 + 2\epsilon)(\epsilon - n^2)}{\epsilon(n^2 + 2)^2}\frac{M}{D}$$

Böttcher[18] calculated μ for a number of liquids and obtained values agreeing reasonably well on the whole with those reported for the gaseous molecules. It seemed worth while to subject our data to a similar treatment to estimate the dipole moments, and in particular the relative dipole moments, of the diastereomeric pairs we studied.

Since between the members of each pair of these isomers ϵ differs much more than the other parameters appearing in Onsager's equation, the difference in the calculated μ's between isomers is in the same direction as the difference between ϵ's. We used n^{25}D for n; the dipole moment values thus calculated are tabulated below.

Compound	Dipole moment of the *meso* or *dl-erythro* isomer		Dipole moment of the *dl* or *dl-threo* isomer
2,3-Diacetoxybutane	2.35	>	1.95
2,3-Diacetoxypentane	2.48	>	2.07
3,4-Diacetoxyheptane	2.68	>	2.18
2,3-Dibromobutane	1.73	>	1.62
2,3-Dibromopentane	1.67	<	1.90
3,4-Dibromohexane	1.57	<	2.06
2-Acetoxy-3-bromobutane	2.23	≈	2.26

It has been pointed out by Dr. V. Schomaker that the dipole moment of ethylene dichloride calculated by means of Onsager's theory from the dielectric constant of the liquid is considerably greater than the dipole moment of a molecule in the gas at the same temperature, and that this fact probably indicates that the relative abundance of the *cis* and *trans* forms of ethylene dichloride in the liquid is quite different from the relative abundance in the gas. The same effect may be expected to occur in the liquids discussed in the present paper; the dipole moments which we have calculated may, for this reason, differ appreciably from those of the corresponding free molecules.

Moreover, it is conceivable, but not probable, that molecular association[17] in some of the liquids affects the dielectric constants of the members of

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(12) Sherrill, Smith and Thompson. THIS JOURNAL, **56**, 611 (1934).

(13) Boord and co-workers, THIS JOURNAL, **52**, 651 (1930); **53**, 1505 (1931).

(14) Trieschmann, *Z. physik. Chem.*, **B33**, 283 (1936).

(15) Wyman, THIS JOURNAL, **58**, 1482 (1936).

(16) Onsager, *ibid.*, **58**, 1486 (1936).

(17) J. N. Wilson, *Chem. Rev.*, **25**, 377 (1939),

(18) Böttcher, *Physica*, **6**, 59 (1939).

a diastereomeric pair enough differently to lead to an erroneous conclusion as to which member has the higher dipole moment. Pertinent to this question are Stewart's findings[19] that in the cases of diethyl tartrate, pinene and camphene the *dl* mixtures possess the same dielectric constants as the corresponding *d* or *l* compounds.

Despite the uncertainties and approximations involved in computing dipole moments from the dielectric constants of pure liquids it seems probable that the values tabulated above indicate correctly both the approximate dipole moments of the diastereomers and the sense of the difference between the dipole moments of the members of a pair of isomers.

While any extended discussion of the significance of the relative dipole moments of the pairs of diastereomers we have investigated should await actual quantitative work on the dipole moments, several things may be pointed out at this time. It would seem that the order *meso* > *dl* and the analogous one *erythro* > *threo* are much more prevalent than has been indicated by the previous literature. The dipole moments of the diethyl tartrates, the dimethyl α,α'-dimethoxysuccinates, the dimethyl α,α'-dichlorosuccinates, the hydrobenzoins, and the stilbene chlorides have been reported previously.[20,21] In these cases only the diethyl tartrates exhibit the order of dipole moments *meso* > *dl*, and the difference in dipole moments is very large only for the stilbene chlorides. Judging from dielectric constants it would appear that in the cases investigated by us the differences between dipole moments of isomers are not very large. Except for the dibromobutanes, the compounds which exhibit the order *meso* > *dl* seem to be the ones with angular polar groups.[2]

The relative dipole moments of diastereomers such as the 2,3-dibromobutanes depend on both the equilibrium configurations about the central carbon–carbon bond and the vibrations or rotations about this bond. Thus, the customary expectation that the *meso* isomer will have the lower dipole moment seems difficult to justify. For example, in the case of the 2,3-dibromobutanes, electron diffraction studies[22] have shown that the equilibrium configuration for both the *meso* and *dl* isomers is that with the bromine atoms *trans* to each other. Thus, the equilibrium *meso* molecule has zero moment and the equilibrium *d* or *l* molecule has a small moment. The rather large moment of this type of molecule then arises chiefly from vibrations about the mean configuration. The shape of the potential curve is different for the *meso* and *dl* compounds because different interactions are involved in the vibration about the mean position. Thus, it is conceivable that either order, *meso* > *dl* or *dl* > *meso* is possible for diastereomeric pairs.

Acknowledgment.—We wish to acknowledge our gratitude to those already mentioned as having furnished chemicals, and also to Professor Linus Pauling and particularly to Dr. J. Norton Wilson for criticisms and suggestions.

Summary

The dielectric constants of seven pairs of diastereomers, namely, the 2,3-diacetoxybutanes, 2,3-diacetoxypentanes, 3,4-diacetoxyheptanes, 2,3-dibromobutanes, 2,3-dibromopentanes, 3,4-dibromohexanes, and 2-acetoxy-3-bromobutanes, have been measured. In general, the members of a pair of diastereomers differ sufficiently in their dielectric constants for the dielectric constant to be useful for analytical purposes.

From these dielectric constants dipole moments have been estimated using Onsager's equation. The ϵ's and μ's for *meso* and *erythro* compounds are compared with those for the corresponding *dl* and *threo* isomers.

PASADENA, CALIFORNIA RECEIVED DECEMBER 12, 1939

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[19] Stewart, *J. Chem. Soc.*, **93**, 1059 (1908).

[20] Stefan Goldschmidt, "Hand- und Jahrbuch der chemischen Physik, 4. Stereochemie," Akademische Verlagsgesellschaft m. b. H., Leipzig, 1933, p. 52, for a summary.

[21] Eisenlohr and Hill, *Z. physik. Chem.*, **B36**, 30 (1937).

[22] Stevenson and Schomaker, THIS JOURNAL, **61**, 3173 (1939).