I. THE PREPARATION AND PHYSICAL PROPERTIES OF CRYSTALLINE LITHIUM ALKYLS

II. THE INTEGRATED INTENSITY OF THE INFRARED ABSORPTION BAND DUE TO O-H STRETCHING IN ALIPHATIC ALCOHOLS

By

Theodore L. Brown

A THESIS

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VITA

Theodore L. Brown

Candidate for the degree of

Doctor of Philosophy

Major Field: Physical Chemistry

Minor Fields: Mathematics, Physics

Biographical:

Born October 15, 1928 in Green Bay, Wisconsin.

Undergraduate Studies at the Illinois Institute of Technology, Chicago, Illinois, 1946-50.

Graduate Studies at Michigan State University, 1953-56.

Experience:

Graduate Assistant in Chemistry at Michigan State University, 1953-56; United States Navy, 1950-53.

Member of the American Chemical Society; Member of Phi Lambda Upsilon and Sigma Pi Sigma; Associate Member of Sigma Xi.

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ABSTRACT

Methyl- and ethyl-lithium have been prepared as pure crystalline materials. A new method for the synthesis of methyl-lithium is much simpler than the previous method, and gives a material of at least 95% purity. This method involves the addition of methyl iodide to ethyl-lithium in benzene solution.

X-ray diffraction data for the crystalline materials were used in establishing the crystal class and unit cell dimensions for both materials. When used in conjunction with the results of microscopic observation the x-ray data permit the unambiguous determination of the space group for ethyl-lithium crystals. Methyl-lithium is of cubic symmetry, unit cell dimensions 8.909 ± 0.016 Å, 16 molecules per unit cell. Ethyl-lithium is orthorhombic, unit cell dimensions, ao = 665 Å, b_o=9.06 Å, c_o=8.10 Å, 8 molecules per unit cell, space group $P222_1$.

Investigation of benzene solutions of ethyl-lithium reveals that the ethyl-lithium is highly associated in solution. The formation of distinct covalent bonds on association is indicated.

The observed sum of atomic and orientation polarizations for the solute in these solutions is considered to be due in some measure to atomic polarization; the electric moment of the polymeric molecule is probably not less than 1.6 Debye.

PART I

THE PREPARATION AND PHYSICAL PROPERTIES OF CRYSTALLINE LITHIUM ALKYLS

INTRODUCTION

The lithium alkyls to be discussed here are members of a large class of compounds known as organometallic. An organometallic compound is defined as one in which there exists a direct carbon-to-metal bond (1).

Although the first preparation of an organometallic compound was made by Frankland in 1849 (2), the first preparation and isolation of lithium alkyl was not done until 1917 when Schlenk and co-workers prepared a number of these compounds (3). The reaction employed by these early workers involved the action of an alkali metal on the appropriate mercury or zinc dialkyl, the reaction being carried out in benzene. It was noted in these early papers that the compounds were in general extremely sensitive to oxygen and moisture, inflaming spontaneously in air.

In 1924 Hein and others studied the behavior of alkali metal alkyls in dimethylzinc and trimethylaluminum as solvents (4). It was concluded from these studies that the alkali metal alkyls were salt-like in their behavior in these solvents, since their solutions showed good conductivity. It was also noted, however, that fused ethyl-lithium and solutions of ethyl-lithium in benzene did not show any appreciable conductance. Current opinion on this work is that the conductivity which the solutions exhibit is due to a solvolytic reaction which produces complexes of the type $MZnR_3$ which ionize (5).

Since lithium alkyls are closely related to the corresponding alkyl Grignard reagents, it was realized early that the lithium compounds might be of considerable value as a synthetic tool in organic reactions. K. Ziegler and co-workers succeeded in making them available for these purposes by devising methods of preparation which closely parallel those used in making the Grignard reagents (6). The previously used methods involving zinc or mercury dialkyls were not suitable because of the flammability of the zinc compounds and the toxicity of the mercury compounds.

The methods of preparation devised by Ziegler were further developed in this country by Gilman (7). The preparations involved the reaction of the appropriate alkyl halide with lithium metal in benzene or ether as solvent. The general reaction is of the form

$$2Li + R - X \longrightarrow R{-}Li + LiX$$

The lithium alkyl which is produced by the reaction is formed in solution and is used in further reactions without removal from the reaction medium.

These preparatory methods were quite successful and provided for a considerable increase in the use of lithium alkyls in organic synthetic work. It is interesting to note, however, that while the uses of these compounds in synthesis increased tremendously, there was little work done to investigate the nature of these solutions or the properties of the pure lithium alkyls. A similar situation has existed in the case of the Grignard compounds, although there the complex nature of the system made any studies of this nature doubly difficult.

Since the present study is concerned with the properties of the lithium alkyls as pure compounds, and with the physical properties of their solutions, no attempt will be made to review the vast literature which exists on their reactions with organic compounds. This material has received several excellent reviews, of which those of Gilman (1) and Braude (8) are perhaps most complete and up to date. The work done on the physical properties of these compounds and their solutions is not extensive. Table I is a summary of all the existing information on the simple alkyls.

In most of the studies involving the pure compounds the lithium alkyls have been prepared by the reaction of the appropriate dialkyl mercury with lithium metal in benzene. In preparing methyl-lithium, however, dimethylmercury is caused to react with ethyl-lithium in benzene:

$$Hg(CH_3)_2 + 2C_2H_5Li \longrightarrow Hg(C_2H_5)_2 + \underline{2CH_3Li}$$

The methyl-lithium which is formed, being insoluble in benzene, settles to the bottom as a micro-crystalline precipitate.

In preparing pure n-butyl-lithium Ziegler made use of the reaction of n-butyl chloride and lithium metal (9). In 1953 T. V. Talalaeva prepared ethyl-lithium by reaction of ethyl bromide with lithium metal in pentane, followed by crystallization from the reaction solvent (10). The material thus obtained was filtered and purified by recrystallization

TABLE I

PHYSICAL PROPERTIES OF LITHIUM ALKYLS

Methyl-lithium -	Colorless, infusible solid. Insoluble in benzene, petroleum ether, but moderately soluble in ethers (3). Solution in phenetole stable at 150°C. for prolonged periods (24).
Ethyl-lithium -	Colorless solid, melting point 95°C. with some decomposition (3). Can be sublimed at 95°C. under high vacuum (9). Soluble in ethers, benzene; moderately soluble in pentane (3).
n-Propyl-lithium -	Colorless liquid, very low vapor pressure. Soluble in benzene, ethers (3,24).
n-Butyl-lithium -	Colorless liquid. Vapor pressure at 60°C., 4×10^{-4} mm. Estimated heat of vaporization, 33 kcal/mole (25). Associated 6-7 fold in benzene (25). Distillable under high vacuum (9). Density at room temperature 0.77 gm./ml.(9). Electric moment in benzene solution, 0.97 Debye (26).

from hexane. All reactions were carried out in a closed glass system. While the method did yield pure ethyl-lithium, it did not lend itself readily to further handling of the material in connection with studies of the pure crystals. One of the goals of the present study has been to modify the existing methods or to develop new ones for the preparation of pure lithium alkyls so that they may be obtained under conditions which permit subsequent operations to be carried out on them.

A study of the physical properties of the lithium alkyls is part of the larger problem involving metal alkyls in general. Examination of the existing body of knowledge regarding this class of compounds reveals sharp differences in properties and behavior which provide a basis for further classification. The alkyls of the metals of the first three groups of the periodic table show markedly different behavior from other metal alkyls. There are, on the other hand, remarkable similarities among the compounds of these groups. Table II shows the properties of some representative compounds, with dimethylamine included for comparison. Coates, in reviewing the existing knowledge of these compounds has pointed out the properties which they exhibit are not easily explained in terms of the simpler ideas of valency (11).

TABLE II

PHYSICAL PROPERTIES OF SOME GROUP I, II AND III METAL ALKYLS

Compound	State	Melting, Boiling Point, °C.	Association	Complexes	Comments
$B(CH_3)_3$(11)	gas	b.p. -20	monomeric	with electron donors	planar, boron bonding sp^2
$Al(CH_3)_3$(11)	liquid	m.p. 15	dimeric in solution and in the vapor phase	etherate	bridge structure
$Be(CH_3)_2$(11)	solid	sublimes 200	associated in solution and in the vapor phase	di-etherate	ht. of sublimation about 22 kcal. per mole
$Be(C_2H_5)_2$(8,11)	liquid	b.p. 180 w. decomp.	-----	di-etherate	-----
$Mg(CH_3)_2$(8)	solid	non-fusible	-----	ether-distillable	stable to 200-250° C.
$Mg(C_2H_5)_2$(8)	solid	non-fusible	-----	ether-distillable	stable to 200-250° C.
NaR(8)	solid	non-fusible	-----	-----	
$Zn(CH_3)_2$(8,11)	liquid	b.p. 44	monomeric	-----	linear molecule, zinc bonding sp
Li R	see Table I				

THEORY

One approach to the valency problem presented by these compounds is that of R. E. Rundle, who has characterized them as electron-deficient (12,13). An electron-deficient compound may be described as one in which the number of bonds formed in making up a structural unit exceeds the number of electron pairs available for bonding. Perhaps the simplest examples of electron-deficient bonding are the metals, in which each metal atom is bound to many neighbors by means of electron pairs which resonate among the various bond positions (14). The type of electron-deficient bonding which Rundle proposes for the metal alkyls as well as some other classes of compounds is of a different form, however, from that which Pauling uses in his theory of metals. In the former instance an electron-deficient compound is described as one which contains a set of atoms A having unfilled orbitals in the valency shell (metal atoms), and a set of atoms B which utilize the unfilled A orbitals in bond formation by use of one or more of their own orbitals for more than one bond. The bonds thus formed are of a fractional bond order.

As an example, in trimethylaluminum the aluminum atom possesses four orbitals, only three of which would be utilized in forming $Al(CH_3)_3$ monomer. The compound has been shown to be a dimer in solution, however (15), and the crystal structure of the dimer has been determined, showing that it possesses a bridge structure with methyl groups occupying the bridge positions (16). Rundle proposes that the tetrahedral orbitals from the bridge carbons are directed between the metal atoms, and that bonding occurs as a result of overlap of each of these carbon orbitals with the two tetrahedral metal orbitals directed toward it. A three-center bond is thus established, involving the use of one carbon orbital in bonding with two metal orbitals. The Al-C distance for the bridge carbons is 2.24 Å, compared with 1.99 Å for the Al-C distance to the outside methyl carbons; the larger distance for the bridge bonds is in keeping with their fractional bond order. A schematic diagram of the bonding atomic orbitals in the four-membered ring, taken from Rundle's paper, is shown in Figure 1.

A similar structure has been found for dimethylberyllium, in which the beryllium atoms are tetrahedrally surrounded by methyl groups (17). Another example among the metal alkyls is that of platinum tetramethyl tetramer, in which each platinum atom is octahedrally surrounded by methyl groups (18). It may be said from these examples that metal alkyls tend to assume a configuration in which the metal atom utilizes all of the valency shell orbitals in bonding. In the case of the alkali metal alkyls this would involve the formation of three additional bonds per metal atom via electron-deficient bonding.

It is possible to generalize to some extent on the conditions which will lead to formation of electron-deficient bonds of the type proposed by Rundle (13). The first condition, as stated a little differently from above, is that there be a set of atoms A which have fewer valence electrons than stable orbitals, and a set B which cannot use the extra bonding orbitals of the A atoms without using some of

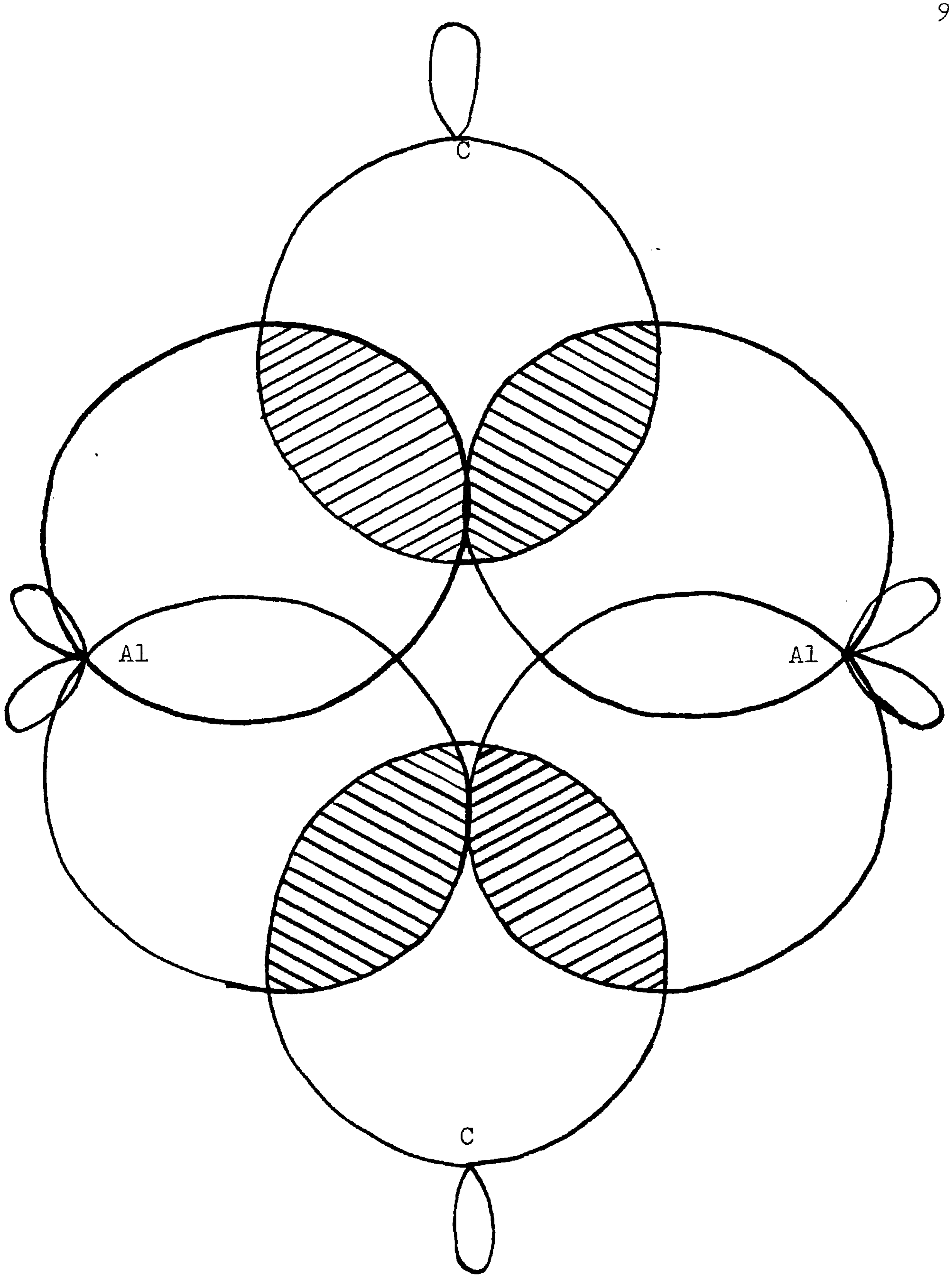


Figure 1. Arrangement of bonding atomic orbitals in trimethylaluminum dimer ring.

their own bond orbitals for more than one bond. Thus a compound such as beryllium dichloride, iso-structural with the dimethyl compound, is not an electron-deficient compound, because the bond which the chlorine atoms form with the second metal atom is merely an electron donor bond involving one of the unshared electron pairs on the chlorine.

The second condition concerns the electronegativities of the atoms involved in the electron-deficient bonding, and can best be seen in terms of the simple system of atoms A, A' and B shown in I and II.

$$\underset{\text{I}}{A' - B \quad A} \qquad\qquad \underset{\text{II}}{A' \quad B - A}$$

The stability of the three-center bond which is formed through resonance between structures I and II is determined by the symmetry of the arrangement. The stability will be greatest when all three atoms are the same, as in H_3^+. When the arrangement is symmetrical, with B different from A and A', a stable arrangement would still obtain, the stability perhaps being greatest when the electronegativity of B is closest to that of A and A'. When all three atoms are different, it is to be expected that the arrangement will be most stable when the B-A and B-A' bonds are closest in bond strength.

The third condition which must be met is that of correct spatial arrangement of bonding orbitals. Whatever orbitals are used by the carbon atoms in forming the electron deficient bonds in the metal alkyls, there must be overlap of these orbitals with those of the metal atoms.

It is of interest to examine the existing information on the groups I, II and III metal alkyls in the light of these conditions. The first requirement is of course met, the metal atoms having otherwise unfilled orbitals available for bond formation. The second condition is met to a fair degree for most of the metals under discussion, with the possible exception of the alkali metals other than lithium. Table III shows the electronegativities of some of the metals along with the values for carbon and hydrogen, as taken from a recent review (19). A three-center bond with carbon as the center atom and hydrogen and the metal as the A and A' atoms would be unsymmetrical with respect to electronegativities. It is reasonable to expect that if the electron-deficient bonding were of this type it would be least stable with metals of lowest electronegativity. It will be pointed out later in more detail that the reverse is apparently true. There is no evidence at present to support the idea that the methyl hydrogens are involved in electron-deficient bonding in the metal alkyls (16). A bond which involved carbon as center atom and two of the metal atoms as end atoms would of course always be symmetrical. It is a bonding of this type which Rundle had proposed for the aluminum and beryllium compounds previously mentioned. Although it is not possible to predict with certainty how the stability of this type of bond will depend on the electronegativity of the metal atoms it would seem from consideration of all the possible contributing structures that the bond would be most stable when the metal electronegativity is closest to that of carbon. It is very likely not strongly dependent on this variable in any case.

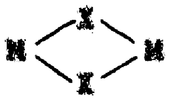
TABLE III

SOME ELECTRONEGATIVITY VALUES (19)

Element	Electronegativity
Carbon	2.5
Hydrogen	2.1
Boron	1.9
Aluminum	1.5
Beryllium	1.4
Magnesium	1.2
Lithium	1.0
Sodium	0.9
Potassium	0.8
Zinc	1.5

It is worth-while to examine the data in Table II with the considerations which have been discussed above in mind. It will be noted, for example, that trimethylboron does not form electron-deficient bonds. Further, in going downward in any one periodic group it is seen that the extent of electron-deficient bonding appears to increase. That is, in comparing the compounds of boron with aluminum, beryllium with magnesium or lithium with sodium there appears in each case to be a considerable increase in the extent to which the materials are polymerized, as evidenced by melting and boiling points, and by thermal stabilities. This relationship would not have been predicted from considerations of electronegativity alone; if anything, the reverse might have been expected, since the metal electronegativities are further removed from that of carbon in going downward in any one periodic group.

The agreement of known structures with the third condition, that of correct spatial arrangement of the bonding orbitals, provides interesting material for discussion. There have been three structures determined which are of interest here; these are diborane, B_2H_6, the trimethylaluminum dimer and the dimethylberyllium polymer. In all three cases a four-membered ring of the form



is formed, where X represents hydrogen in the case of diborane and carbon in the case of the aluminum and beryllium compounds; M represents the metal atoms. The pertinent data on bond angles and distances in the ring are summarised in Table IV.

It will be noted first that the metal-metal distances are quite short. From consideration of a large number of structures Pauling had developed a table of covalent radii for metals as well as an expression relating bond length to bond order (14). The expression is

$$R(1) - R(n) = 0.30 \text{ Log } n$$

where R(1) is the sum of the covalent radii for the two atoms involved in the bond, R(n) is the observed interatomic distance, and n is the calculated bond order. This expression is best considered as a rough rule, since the value of 0.300 is a best value from among a number of possible values. If the values of the metal-metal distances in the three structures above are inserted in this expression, metal-metal bond orders of about 0.5, 1.0 and 0.4 are obtained for the boron, aluminum and beryllium compounds, respectively.

Metal-metal bonding has been stressed in connection with the structure of the boron hydrides (20,21,22), although this factor has been ignored in recent work done in interpreting the character of the bonding in terms of three-center bonds (23).

Rundle admits that in the case of the aluminum compound some metal-metal bonding is likely, but his approach in general has been to minimize its importance, and to argue that the small metal-metal distances are the result of a configuration which derives its stabilization from the three-center bond formed between carbon and the two metal atoms.

TABLE IV

SUMMARY OF BOND DISTANCES AND ANGLES IN FOUR-MEMBERED RINGS

	B_2H_6(29)	$Al(CH_3)_3$(16)	$Be(CH_3)_2$(17)
M-M distance	1.77A	2.55A	2.09A
M-X distance	1.33A	2.24A	1.93A
M-X-M angle	?	70°	66°
X-M-X angle	100°	110°	114°

The small M-C-M angle is thus considered to be a consequence of the fact that this arrangement gives good overlap of the two metal orbitals with the one carbon orbital which lies between them.

With such short intermetallic distances, however, it is difficult to picture an arrangement in which there is not some overlap of the metal orbitals, corresponding to metal-metal bonding.

The relative stabilities of the metal alkyls afford some interesting considerations when viewed in the light of spatial or steric considerations. For the purposes of this discussion the radii of some of the metals, taken from Pauling's table, are listed in Table V.

It has already been remarked that although boron hydride forms an electron-deficient dimer, trimethylboron does not. The trimethyl compound does form stable complexes with electron-pair donor molecules, however, in which the hydridization about the boron atom is presumably tetrahedral. The failure of the trimethyl compound to form an electron-deficient dimer is undoubtedly caused by steric repulsions due to the large size of the methyl groups relative to the radius of the boron atom. Similarly the apparently greater degree of polymerization of the magnesium alkyls as compared with those of beryllium is probably due to the larger radius of magnesium.

These steric effects may be interpreted in either of two ways. If the three-center bond is accepted as being of primary importance in electron-deficient bonding, the steric effects must be considered as preventing the formation of a more stable configuration as far as orbital overlap is concerned. It is not possible at present to predict just

TABLE V

SOME VALUES OF METALLIC RADII (IN Å) (14)

A-Group Metals		B-Group Metals	
Li	1.22		
Na	1.57		
K	2.02	Cu	1.17
Be	0.89		
Mg	1.36		
Ca	1.73	Zn	1.25
B	0.78		
Al	1.25		
Sc	1.44	Ga	1.25

where in the structure these steric effects would be most important, but the example of trimethylboron can be used to illustrate the point in a general way. In a hypothetical structure for $B_2(CH_3)_6$ one would expect that the B-C-B angle in the ring would be small, as is the case for the aluminum and beryllium compounds. This would in turn result in a C-B-C angle of about 120°. Even without knowing precisely what value to take for the effective radius of the methyl groups (1.73 A has been given in connection with other studies of steric effects (28)) it is readily seen that a structure of this type would lead to strong steric interactions between methyl groups.

An alternative view of this steric effect would be to suppose that the repulsive interactions operate to prevent the metal atoms from approaching one another closely enough to give good metal-metal bonding, and that this factor is of sufficient importance to determine the stabilities. It will probably not be possible to resolve the question of the relative importance of the alternative types of bonding in these compounds until the structures of more metal alkyls have been determined.

It is interesting to note that the alkyls of metals with filled d subshells have little or no tendency to form electron-deficient bonds. Perhaps the best explanation for this is that repulsions due to filled d orbitals prevent the attainment of metal-metal distances which are small enough to give configurations which would be suitable for electron-deficient bonding. It is to be noted that the metal-metal distances in these electron-deficient compounds are smaller than those encountered in metallic structures.

EXPERIMENTAL

Dry Box Construction and Operation

The dry box used in the handling of lithium alkyls is similar in general construction to others which have been described (29). A number of new features were incorporated into its design and operation, however, which are worth relating. A photograph of the box is shown in Figure 2. It is constructed of 16 gauge galvanized sheet iron with the seams riveted every two inches and soldered to give an airtight casing. The window is of Plexiglass drilled to fit on threaded studs placed every two inches around the edge. A gasket of 1/16" rubber was placed between the window and the box; the window was pressed tightly against this gasket by nuts on the threaded studs. A soft sealing compound was applied to both sides of the gasket before the window was pressed into place. A fluorescent lighting fixture was used for illumination in the box. The fluorescent lamp passes through a heavy-walled glass tube of slightly larger diameter; the airtight seal with the walls of the box is made on the outside of this heavy tubing, thus eliminating any stress on the light fixture.

The details of the way in which this seal is accomplished are shown in Figure 3; the packing gasket is of the type commonly available for plumbing applications.

The box is built in two compartments; the lower one is used in transferring materials in and out of the box without seriously contaminating the atmosphere in the box. A one-foot-square port on the

Figure 2. Dry Box

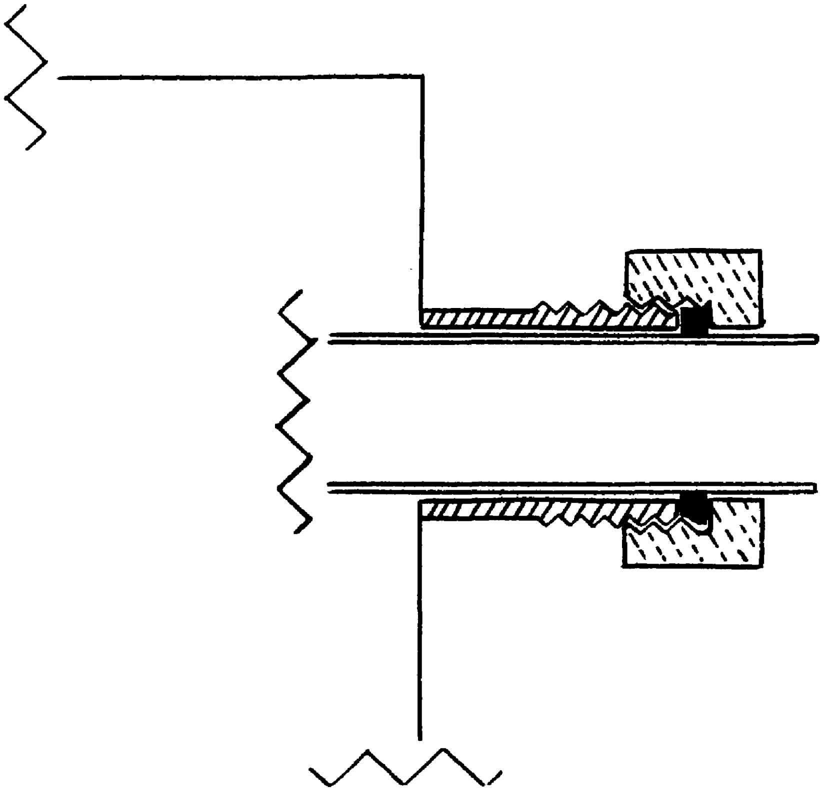


Figure 3. Details of seal of light-fixture tube on the dry box.

floor of the upper box connects the upper and lower chambers. Around the edge of this port there is a trough 1/2" by 1/2" which is filled with Apiezon-W wax, a black, non-volatile solid of putty-like consistency. The port door is constructed of 16 gauge sheet metal and has a 1/2" knife edge running around its lower side of such dimensions that when the door is placed down over the port the knife edge coincides with the center of the trough. By pressing the door down into the wax an airtight seal is created, thus isolating the lower compartment from the upper.

The outer door also consists of a one-foot-square port. The trough which surrounds it is nine inches high, however, as is the vertical edge on the lower side of the outer port door. This trough contains mineral oil up to about a five inch level. When the door is dropped down into the trough a liquid seal is formed.

Attached to the top of the box is a gasometer device, illustrated in Figure 4. The purpose of this device is to permit changes in the volume of the box occasioned by movement of the arms in the gloves, or by loss of gas, without any appreciable change in pressure inside the box. Mineral oil was used as the liquid in the gasometer.

Below the window, on the vertical front of the box, provision for gloves is made in the form of two nine-inch holes with 2" flanges for attaching the gloves. The gloves used were of Neoprene. They were attached to the flanges by stretching them on, then winding tightly with electrical tape.

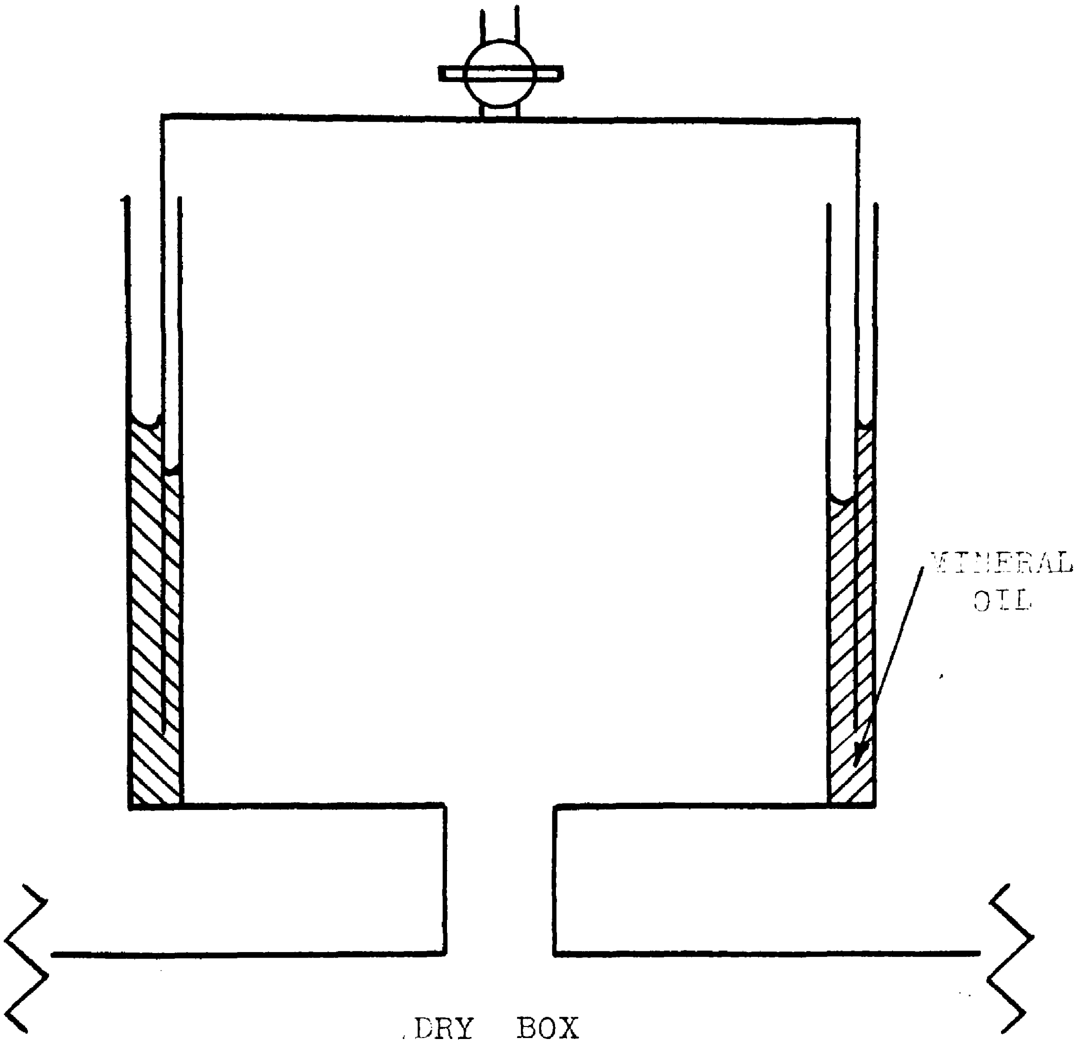


Figure 4. Schematic drawing of gasometer device used on the dry box.

Fittings on the box include six gas-cocks for flushing and pressure release, two 1" outlets on the back wall for leading in aspirator lines or any other desired fittings, and an electrical outlet on the back wall. The inside of the box was well painted, the final coat being white to improve the lighting.

The box was placed in operation for the handling of active materials by flushing it thoroughly with pre-purified nitrogen over a period of an hour or so. All outlet cocks were then closed and the rate of gas flow was adjusted to maintain an appreciable internal pressure. Phosphorus pentoxide was spread into one or two large porcelain dishes, a small blower fan of about 80 cubic feet per minute capacity was operated, and the box allowed to stand for a period of about 24 hours. It was found necessary to stir or add fresh phosphorus pentoxide during the course of the drying period. When the box was thoroughly dry, as evidenced by the behavior of the desiccant, it was ready for use.

It will be noted that except for the initial flushing, no scavenging of oxygen was employed. A copper furnace was employed for some time, the box atmosphere being circulated through it by means of the blower, but this did not prove to be satisfactory. Most of the difficulty arises from the fact that the work done here involved the use of organic solvents. The vapors from these solvents, on passing through the copper furnace, reduce any copper oxide which may be present, producing water. The increased demand on the desiccant did not appear to be compensated for by a marked improvement in the quality of the box atmosphere. Insofar as oxygen content is concerned, thorough flushing of the box appeared to be adequate; pre-purified nitrogen is claimed to have only 0.05% or less oxygen.

One of the most serious problems encountered in the use of a dry box of this type is the diffusion through the gloves. In an effort to reduce the amount of contamination from this source two measures were taken. First, when the gloves were not in use they were tightly rolled up to the glove ports, and the ports covered over with polyethylene sheets held in place with large rubber bands. Secondly, a second pair of gloves were donned and worn inside the box gloves to prevent the considerable moisture which accumulates because of respiration from coming in contact with them. These two measures appeared to be of great help in keeping the atmosphere in the box dry and oxygen-free.

When the box had been thoroughly dried a problem arose because of static electrical effects; these made the handling of dried precipitates very difficult. In order to minimize these effects a very small sample of a high energy gamma emitter was attached to the bottom of the box.

Preparation of Crystalline Lithium Alkyls

During the course of this investigation it was necessary to prepare the lithium alkyls a number of times. The procedure to be followed in relating this aspect of the work will be to describe the method of preparation which was finally arrived at as being the best, and to follow this with remarks on any alternatives which were tried at one time or another.

Ethyllithium — A two-liter, three-neck flask with standard-taper joints was used. A dropping funnel with a tube extending between the upper and lower sections for pressure equalization was used in one of the necks. A stopcock was blown into the pressure equalizing tube, and was used for admission of a stream of pre-purified nitrogen or helium. A precision-bore journal-bearing stirrer with Teflon paddle was placed in the center neck, and a Friedrich's type condenser in the third. The outlet at the top of the condenser was vented to the atmosphere through a drying tower containing barium oxide.

Before beginning the reaction the system was thoroughly dried and well flushed with nitrogen. About 10.5 grams (1.5 moles) of sodium-free lithium in the form of 3/8" rods was beaten out with a hammer to a thickness of about 1/32". These sheets were then cut up with a scissors into pieces about 1/4" wide and the pieces placed in a Waring Blendor jar with about 30-50 ml. of ligroin or other aliphatic hydrocarbon boiling in the range 50-90°C. The covered Waring Blendor was then operated for about 10-15 minutes, after which time the lithium metal was largely in a high state of subdivision. The metal and the solvent were then added to the reaction flask; any required rinsing was done with n-pentane. This solvent is of the 99% purity grade, and need only to be dried before use. The drying was accomplished with calcium chloride followed by phosphorus pentoxide or magnesium sulfate. After addition of the metal to the flask, about a liter of pentane was added, and 51 ml. of ethyl bromide added to the dropping funnel. After thorough flushing the stirrer was placed in operation and about 5-8 ml. of ethyl bromide added to the flask.

The flask was heated with a heating mantle until a moderate amount of reflux was evident. The beginning of the reaction was easily seen, due to the formation of a blue material on the surface of the lithium and in the solvent. As soon as the reaction had begun it was necessary to decrease the heating to keep refluxing from becoming too vigorous. Addition of ethyl bromide was then continued dropwise so that the remainder was added over a period of 3-4 hours. The reaction mixture was stirred for an additional 2-3 hours with very low heating.

On completion of the reaction the condenser was removed under a stream of nitrogen, a side-arm tube was placed in this neck and the top outlet of the condenser attached to this side-arm tube. A two-necked, one-liter flask was then attached to the bottom outlet of the condenser, the vent line to the drying tower being attached to the other neck of the flask; 400 ml. of dried benzene were then added to the flask through the dropping funnel and, with the stirrer in operation, heat was applied to the flask to distill off the lower boiling pentane. Distillation was continued until about 500 ml. of solution remained in the reaction flask. At this time the stirrer was removed and replaced with a stopcock plug, the condenser was removed from the side arm and replaced with a settling tube, and the dropping funnel was replaced with a stopcock plug which is attached to the nitrogen supply. This arrangement is shown in Figure 5. The settling tube was about 50 mm. in diameter, and of such a length as to give it a capacity of about 500 ml.

Most of the solid material in the reaction mixture was allowed to settle, during which time the entire apparatus was flushed with nitrogen

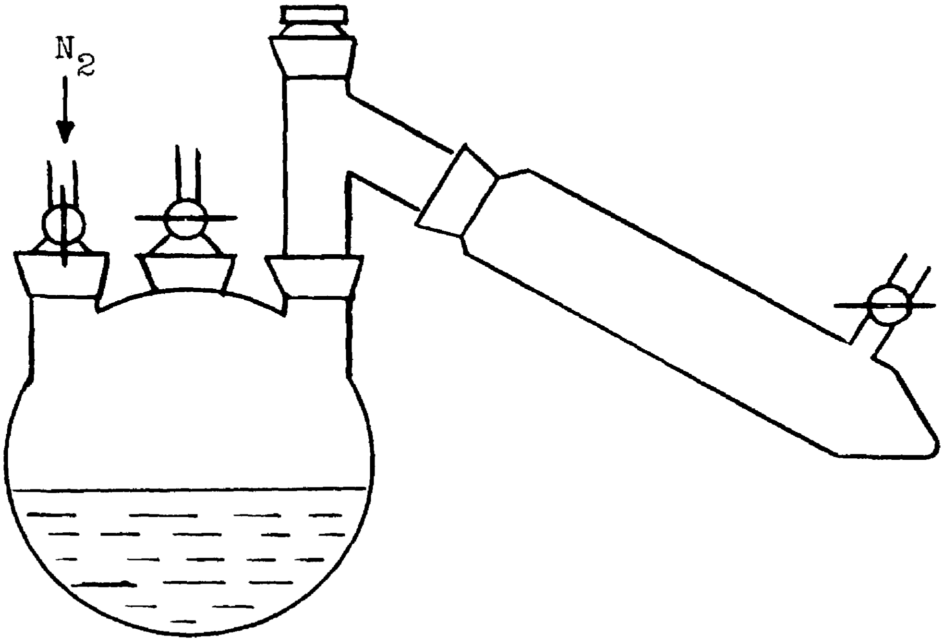


Figure 5. Arrangement for decanting reaction solution into settling tube.

by venting through the stopcock at the bottom of the settling tube. Then, with only the center stopcock open for venting, the apparatus was turned so that the settling tube was nearly vertical, and the solution allowed to run into it until it was full. Most of the solid material remained in the reaction flask during this operation. The settling tube was quickly removed and capped with a glass plug. It was then clamped and allowed to stand for about 24 hours. During this time any suspended matter settled to the bottom below the level of the stopcock.

The solid material remaining in the reaction flask was disposed of by washing it into a large beaker using benzene, allowing it to stand in the hood for a few days, and then cautiously adding an alcohol to decompose any remaining active material.

After the 24 hour standing period the stopcock outlet on the settling tube was connected via a short length of Tygon tubing to a one-liter, three-neck flask with standard-taper joints. The center neck on the flask was connected to the nitrogen supply, the third was connected via two drying towers containing barium oxide and calcium chloride to a water aspirator. After a thorough drying and flushing of the system, the clear solution containing ethyl-lithium was allowed to run into the flask. The connection through which the solution was admitted was then removed and a glass plug inserted. The aspirator was started after adjustment of the nitrogen supply to give a very slow rate of inlet.

It is worth mentioning that in order to avoid contamination of the sample during this reduced pressure operation all connections had to be made airtight. The slow trickle of nitrogen served to purge the system during this time.

As the pressure decreased the solution began to boil. Heat was supplied with a heating mantle to keep the rate of evaporation high. By the time that 75% of the solvent had been removed in this way there was considerable precipitate in the flask. The aspirator line was then pinched off and nitrogen admitted to the flask until atmospheric pressure was reached. The two hose lines leading from the flask were then pinched off tightly, the hoses cut just above the pinch clamps, and the closed flask was ready for transfer to the dry box.

In the dry box the flask was again connected to the aspirator line and suction applied. This was done mainly to chill the solution in the flask, since the temperature coefficient of solubility of ethyl-lithium appears to be quite large. After the flask had been pumped on for some time the suction line was disconnected and the contents of the flask poured through a coarse-grained, sintered glass filter. The solid which collected was dissolved in boiling benzene and the solution poured through a filter. The precipitate of ethyl-lithium which formed when the solution cooled was then filtered from the mother-liquor.

In most cases this single recrystallization was sufficient to give pure ethyl-lithium, but if for some reason it did not, the same procedure was repeated.

In earlier preparations of ethyl-lithium the solution which was drained from the settling tube was concentrated by distilling off the solvent at atmospheric pressure. It was found, however, that at the higher temperatures necessary for this it was quite difficult to avoid decomposition of the ethyl-lithium.

Methyl-lithium — About 100 ml. of 0.1 N solution of purified ethyl-lithium in benzene and 2 gms. of methyl iodide dissolved in about 25 ml. of benzene were used. Both solutions were cooled in the dry box to about 5-10°C., and then mixed together while stirring. A fine white precipitate formed after a few seconds. After about a minute the solution was poured through a medium-grained, sintered glass filter under suction. The precipitate on the filter was washed twice with benzene, and then with pentane to aid in drying.

Since methyl-lithium has not been reported as being made by the above method in any previous work, it was also prepared by the classical method mentioned in the introduction in order to provide material for comparison. This method of preparation involves the reaction of dimethylmercury and ethyl-lithium in benzene, resulting in a precipitate of methyl-lithium.

Dimethylmercury was prepared according to the directions of Marvel and Gould (30). About 40 gms. of purified product boiling in the range 91.5-92.5°C. were obtained. About 5 gms. of this material in 25 ml. of benzene was added to 50 ml. of 0.2 N ethyl-lithium solution in the dry box. A fine white precipitate formed after a few seconds. This material was treated in the same way as the precipitate obtained by the other method.

Several attempts to prepare pure methyl-lithium by use of the reaction of methyl halide with lithium metal in ether as a solvent were unsuccessful. The reaction proceeded well with methyl iodide, but it was not found possible to separate the methyl-lithium formed by the reaction from lithium iodide, which is also a reaction product. A procedure similar to that used in preparing ethyl-lithium was attempted, but a mixture of lithium iodide and methyl-lithium was obtained. Attempts to fractionally crystallize methyl-lithium from the iodide using pentane, benzene or triethylamine were unsuccessful.

Methods of Analysis

Aliquot portions of solutions of lithium alkyls were decomposed with water and titrated with standard acid to yield the amount of total base. To determine the amount of basic material other than lithium alkyl an aliquot portion of the solution was added to a 10% solution of benzyl chloride in ether. A bright yellow color appeared due to the formation of benzyl-lithium. The benzyl-lithium reacted rapidly with a second molecule of benzyl chloride to yield dibenzyl and lithium chloride, thus removing all lithium alkyl from the solution without producing any base. Addition of water and titration with standard acid yielded the net base. This method is not satisfactory for methyl-lithium, which does not react well with benzyl chloride.

Halide ion was analyzed for by decomposing an aliquot portion with water, acidifying with acetic acid and titrating with standard silver nitrate solution, using the appropriate indicator.

In addition to these methods of analysis the results of x-ray diffraction and infrared spectral studies furnished information which was of value in identification and evaluation of purity.

Infrared Spectra

It is necessary, in preparing solids for infrared spectra, to insure that all traces of the solvent from which they are obtained are removed. This was done in this work by placing the solid, while still wet with solvent, in a small side-arm flask fitted with a one-hole stopper and a small separatory funnel. The solid was pumped on for some time using the vacuum pump and then, before the flask was allowed to come to atmospheric pressure, the mulling agent was run into the flask through the separatory funnel. This procedure insured that there would be no contamination of the solid from reaction with the dry box atmosphere.

The solid was then removed from the side-arm flask with a spatula, placed in an agate mortar and ground to the consistency of a cream with the mulling agent. A drop or two of this cream was then placed on a salt plate, and the second salt plate placed over this. The assembly was then clamped in a holder.

All the mulling agents were prepared for this purpose by warming them to at least 100°C. for an extended period of time while bubbling nitrogen through the liquid. Nujol appeared to form good mulls with both methyl- and ethyl-lithium; perfluorokerosene appeared to be satisfactory in mulling with methyl-lithium, but some difficulty was encountered in the case of ethyl-lithium. Perfluorokerosene did not appear to wet the latter compound, and it was not possible to disperse it satisfactorily. By placing a mixture of the compound and mulling agent between salt plates and rubbing them together strongly it was possible to obtain a layer of ethyl-lithium which was thin enough to transmit. The small amount of perfluorokerosene which remained between the plates was sufficient to prevent the immediate decomposition of the solid.

An attempt was made to use fluorolube oil as a mulling agent for ethyl-lithium. This oil is a tetrahalogenated ethylene containing three fluorines and one chlorine atom per structural unit. About thirty seconds after mixing these two materials together, however, a vigorous reaction took place which left a black, carbon-like residue.

Solutions of ethyl-lithium, analyzed for concentration in the manner already described, were loaded into sodium-chloride-window solution cells in the dry box. Matched cells of 0.5 mm. thickness were employed. The cells were cleaned by rinsing with dry benzene. The spectra were recorded on a Perkin Elmer Model 21 recording double-beam infrared spectrometer.

X-ray Diffraction and Microscopic Studies

0.3 mm. diameter lithium borate glass tubes were used to contain the powder samples. Short lengths of this tubing, sealed at the lower end, were mounted in the brass cartridges which fit the holders in the powder cameras.

The solid materials were ground to a fine, dry powder with an agate mortar and pestle. The lithium borate tubes were then carefully filled by immersing the end of the tube in the solid, and then tapping to knock the solid down into the tube. All operations with these fragile tubes are carried out by holding the brass cartridge with a forceps.

The end of the tube was then covered with a small ball of putty and Duco cement applied over this to assure an airtight, mechanically firm seal.

Single crystals of ethyl-lithium were obtained from the recrystallization step in the purification of ethyl-lithium. The crystals were not well formed with respect to face development, but tended for the most part to grow as flat plates of about 0.5 mm. thickness. The crystals were placed in tubes of thin-walled Pyrex or soft glass and the ends of the tubes sealed in the manner described above for the powder samples.

On removal from the dry box the powder samples were mounted in the powder cameras and exposed for periods up to 24 hours. The single-crystal samples were mounted in a Unicam model S.25 goniometer with cylindrical camera. The samples were aligned visually so that the flat sides were vertical; the alignment of the direction at right angles to this was estimated by comparison with the results of microscopic observation (see below). Other exposures were also made of the crystals oriented with the flat sides horizontal. After alignment of the crystals in the goniometer, the cylindrical camera was loaded and placed into position. The goniometer was then placed on the rack provided for it on the x-ray diffraction machine and the sample exposed.

The diffraction machine used was a North American Phillips Model 5001. A copper target was used with a plate voltage of 35KV and a plate current of 16 milliamperes.

Spacings on the powder films were read to an accuracy of 0.05 mm., those on the cylindrical camera films to the nearest 0.5 mm.

For purposes of microscopic observation the single crystals of ethyl-lithium were placed in cavity glass slides and covered with mineral oil and a cover glass. It was not possible by this means to obtain a view of the crystals other than with the flat sides horizontal. In order to permit viewing the crystals from other aspects they were placed in about 1/16" mineral oil in a weighing bottle cover. The crystals were thus protected from the atmosphere; since the density of the crystals is near that of mineral oil, they remain in any desired orientation well enough for purposes of observation.

Methyl-lithium crystals were placed in a cavity glass slide and covered with perfluorokerosene and a cover glass. These crystals were quite small and a variety of orientations was obtained in this way.

The crystals were observed with a Spencer polarizing microscope fitted with Nicol prisms. Both white light and sodium light were used.

Measurements on Benzene Solutions of Ethyl-lithium

The concentrations of all solutions used were determined by the methods previously discussed. The solutions were essentially free of impurities as determined by these analyses.

A 25 ml. pycnometer with side arm markings was calibrated using distilled water. The readings on the side arms were taken while it was immersed in a thermostated bath at a temperature of 25.0°C. The benzene used in the determination of density and dielectric constant was purified by fractional crystallization followed by distillation from phosphorus pentoxide in an efficient fractionating column packed with glass helices.

In determining the densities of the ethyl-lithium solutions the pycnometer was filled with the solution in the dry box, then removed from the box, placed in the bath and the volume at 25.0°C. read. Weighings were done on a Christian Becker Chainomatic balance with a precision of 0.1 mg. The pycnometer was wiped carefully after removal from the bath and allowed to equilibrate in the balance case for about twenty minutes before weighing.

Measurements of dielectric constant were done in an apparatus which has been described elsewhere(31). The heterodyne beat method is employed; a standard capacitance is varied to match changes in the capacitance of the dielectric constant cell occasioned by the introduction of the solutions or solvent. The solutions were loaded in the dry box into a glass bulb to which was attached on the bottom a stopcock and standard taper joint which fit the standard taper joint on the top of the capacitance cell. Match positions were obtained on the standard capacitance for the cell in air, and when filled in turn with pure benzene and with three ethyl-lithium solutions of varying concentration. In order to minimize the possibility of a false reading due to entrapped air, each reading on a liquid was taken as an average of three separate readings, the solution being pushed out and let back into the cell between them. The three values were in good agreement with one another in every case.

The cells used for freezing-point depression measurement are of the type shown in Figure 6. The capacity of the cells is about 30 ml. The smaller tube in the center of the cell is fitted tightly at the top with rubber tubing.

Two cells were used for each measurement. Pure benzene was placed in one cell, the solution in the other. On removal from the dry box the pure benzene cell was chilled until the benzene was about half frozen. The cell was then immersed in a slush of frozen benzene in a Dewar flask. The solution cell was immersed in an ice bath; copper-constantan thermocouples connected in series opposition were then placed in the small diameter tubes and pushed to the bottom. These smaller tubes were made to fit loosely in position and could be moved enough to act as adequate stirrers.

The thermocouples were connected to a Leeds and Northrup amplifier, the output of which was fed into a Leeds and Northrup Speedomax recorder. Because of the small temperature differences measured, the thermocouple output was quite small, and the highest amplification setting of the amplifier could be used. This gave a scale of about 0.12°C. per large division on the chart paper, and permitted readings to the nearest 0.002°C.

The cell containing solution was stirred vigorously as the temperature dropped. After some supercooling there was a sharp rise in temperature, a leveling off, and then a continuing decrease as benzene continued to freeze out. This latter time-temperature line was extrapolated back to the first line to obtain the freezing point. The type of time-temperature curve obtained and the method of extrapolation are shown in Figure 7.

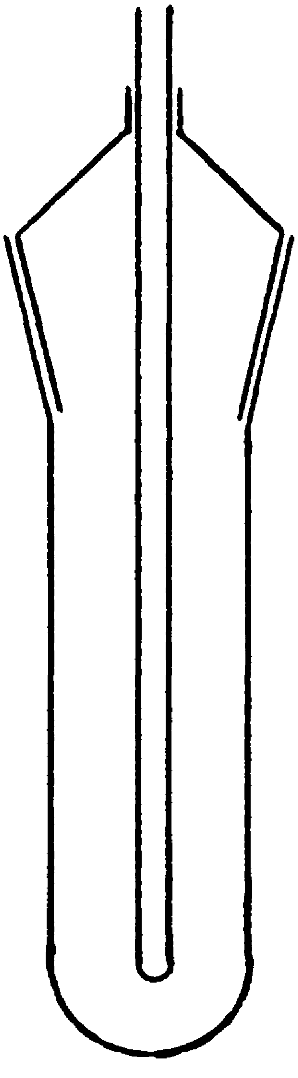


Figure 6. Freezing-point depression cell.

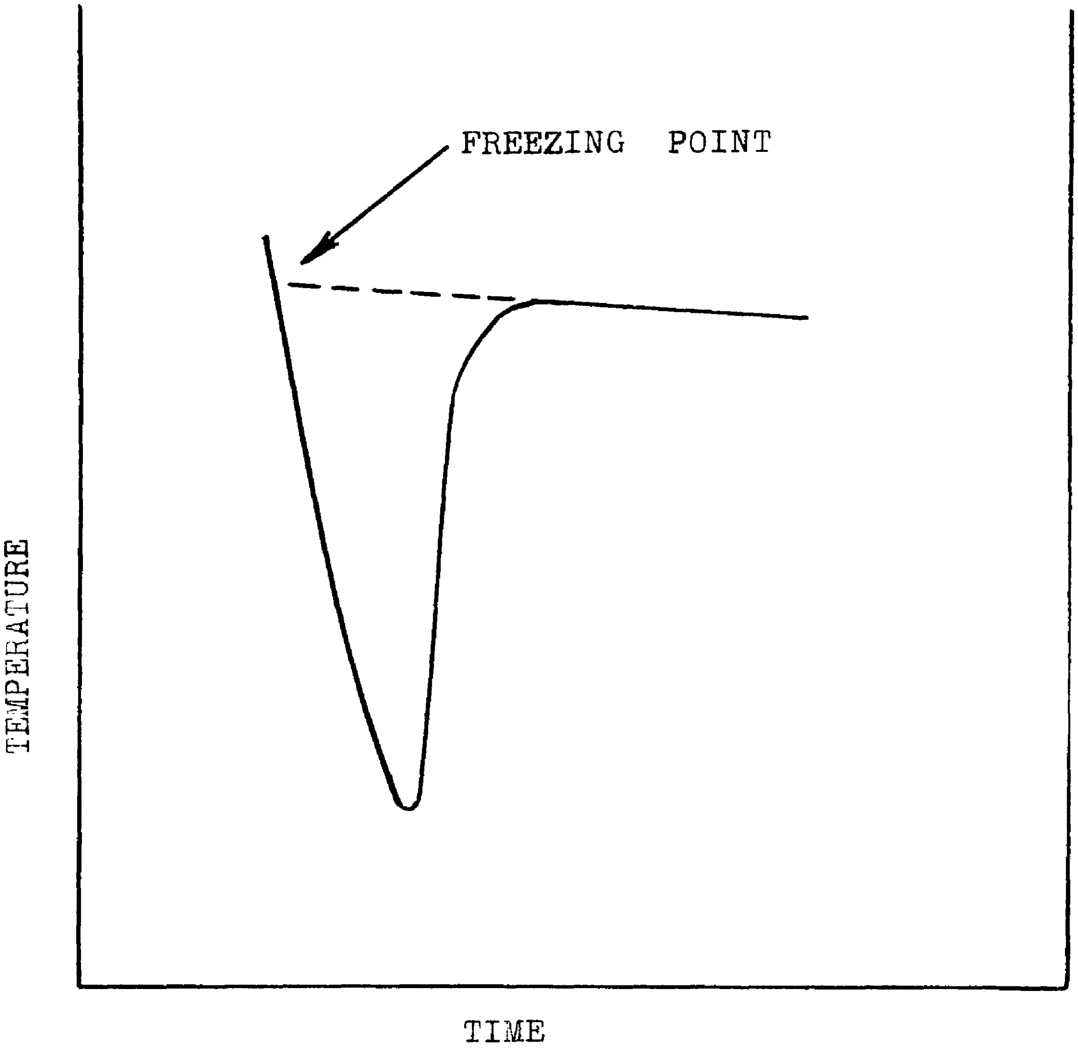


Figure 7. Time - temperature curve obtained in freezing-point lowering experiment.

The thermocouple calibration was made by immersing the low-temperature junction in an ice-water bath and the high-temperature junction in a sodium sulfate-sodium sulfate decahydrate mixture, both reference mixtures being in Dewar flasks. The thermocouple output voltage under these conditions agreed with the table value for this temperature difference.

The temperature stability of the cell containing pure benzene was checked by measuring the thermocouple output as a function of time when the low-temperature junction was immersed in the ice-water bath and the other in the cell. With very little stirring of the benzene cell the output voltage held constant over a 15 minute period to within the accuracy of measurement.

RESULTS

Analysis

The purity of benzene solutions of ethyl-lithium was determined by the methods discussed earlier. Solutions made up from recrystallized ethyl-lithium contained less than 0.5% net base, and gave a negative test for halogen.

In order to determine the amount of decomposition undergone by solid methyl- and ethyl-lithium on exposure to the dry-box atmosphere, ethyl-lithium was ground to a fine powder in a mortar and pestle. This powder was then added to benzene and the analysis carried out as before. When the dry box was thoroughly dry and oxygen-free the amount of decomposition as indicated by the net base content was 2-5%. Since methyl-lithium is less reactive in general than ethyl-lithium, this figure may be taken as an upper limit for both compounds.

In preparing methyl-lithium by the reaction of ethyl-lithium with methyl iodide in benzene, the possibility exists that the coupling reaction will occur, producing propane and lithium iodide. In order to determine the extent to which this reaction occurred a sample of solid methyl-lithium was added to ether and decomposed with water. The base was titrated with standard acetic acid. On completion of the titration a few more drops of acid were added and the iodide titrated using Eosin indicator. The mole percentage of iodide determined in this way was about 5%.

The methyl-lithium produced by the reaction of ethyl-lithium with dimethylmercury was not analysed for purity. The infrared spectra and x-ray diffraction patterns for this material were identical in all respects with those for methyl-lithium produced by the other method.

Infrared Spectra

The infrared spectra obtained for methyl- and ethyl-lithium mulls are shown in Figures 8-11. The spectra of two ethyl-lithium solutions in benzene with appreciably different concentrations are shown in Figures 12 and 13. All of these spectra are drawn from the original data, with the features characteristic of the solvent or mulling agent eliminated in the interest of clarity.

Tables VI-VIII are a listing of the frequencies of the peaks for each of the compounds, with estimates of relative intensity in parentheses. These values of intensity are based on a value of 10 for the most intense maximum on each spectrum.

X-ray Diffraction Data

Table IX lists the value of θ, the reflection angle, and d, the interplanar spacing, for each line of the powder diagram of methyl-lithium. Table X lists the value of θ and $\sin^2\theta$ for each line of the powder diagram for ethyl-lithium. The value of relative intensity, estimated visually, is also given for each line; the values are based on a figure of 10 for the most intense line and 1 for the barely detectable lines.

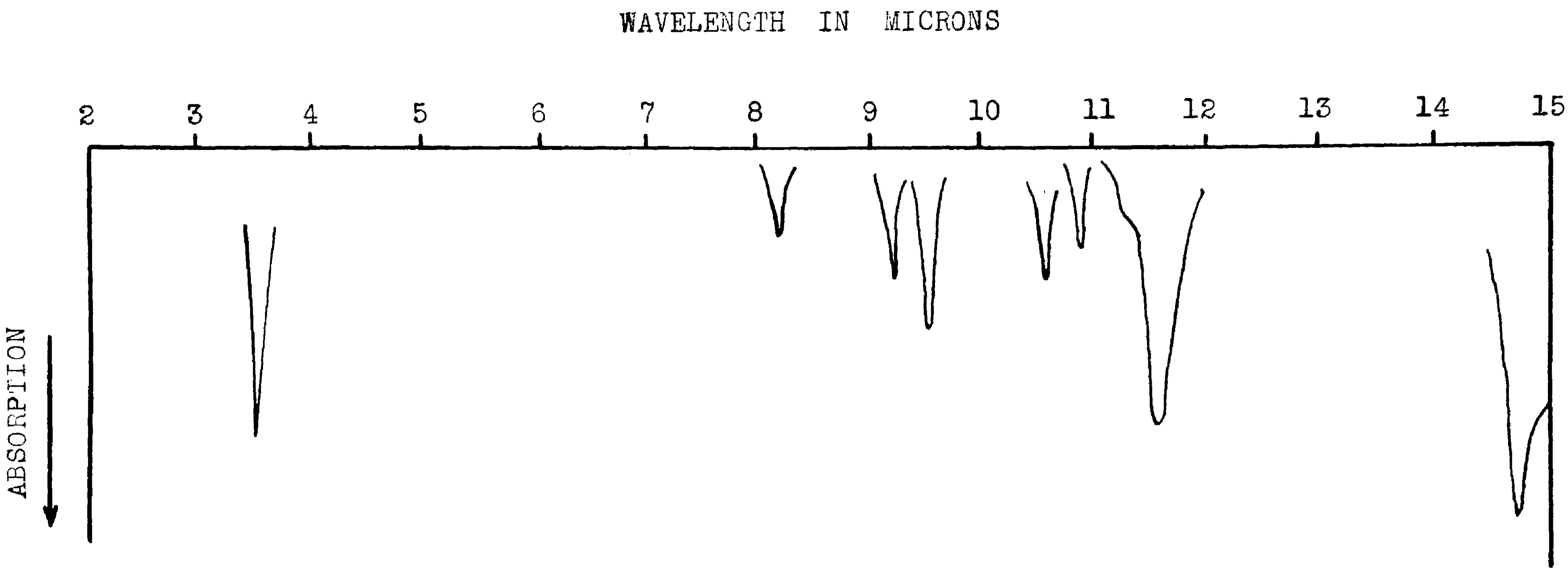


Figure 8. Infrared spectrum of ethyl-lithium in Nujol mull.

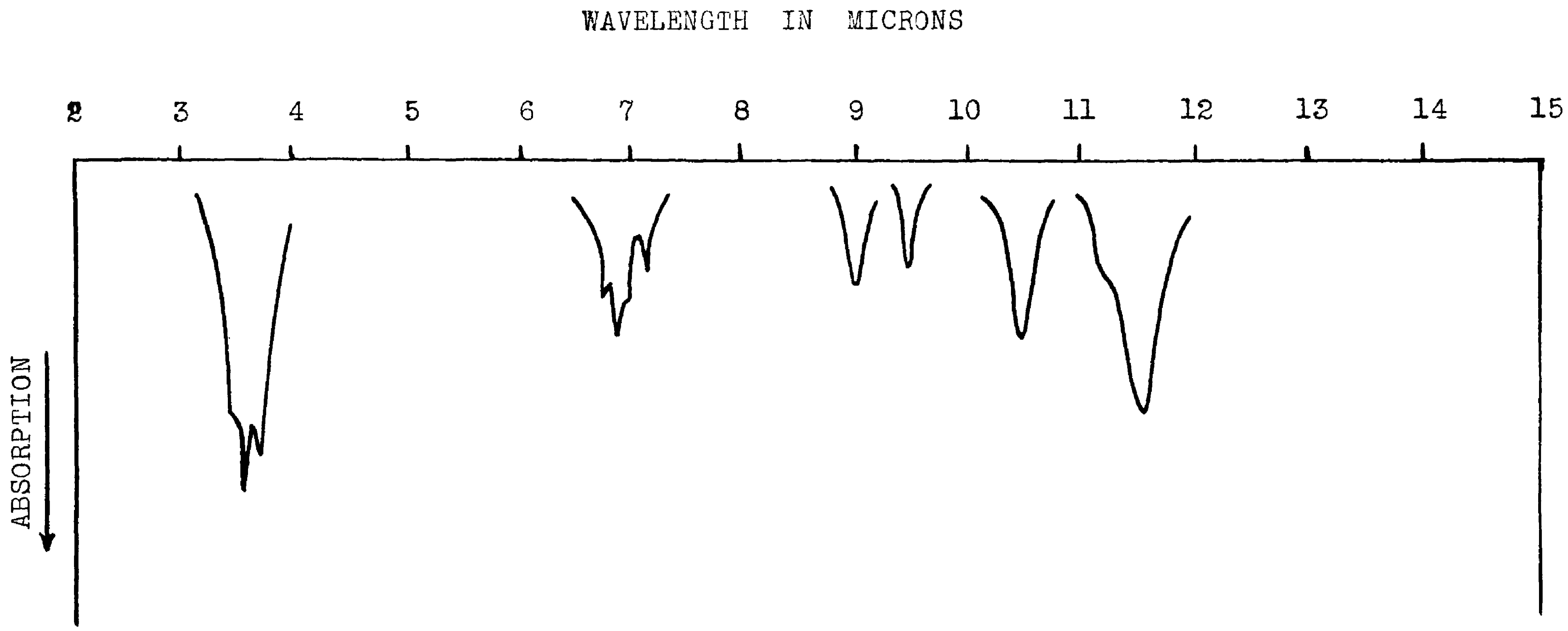


Figure 9. Infrared spectrum of ethyl-lithium in perfluorokerosene mull.

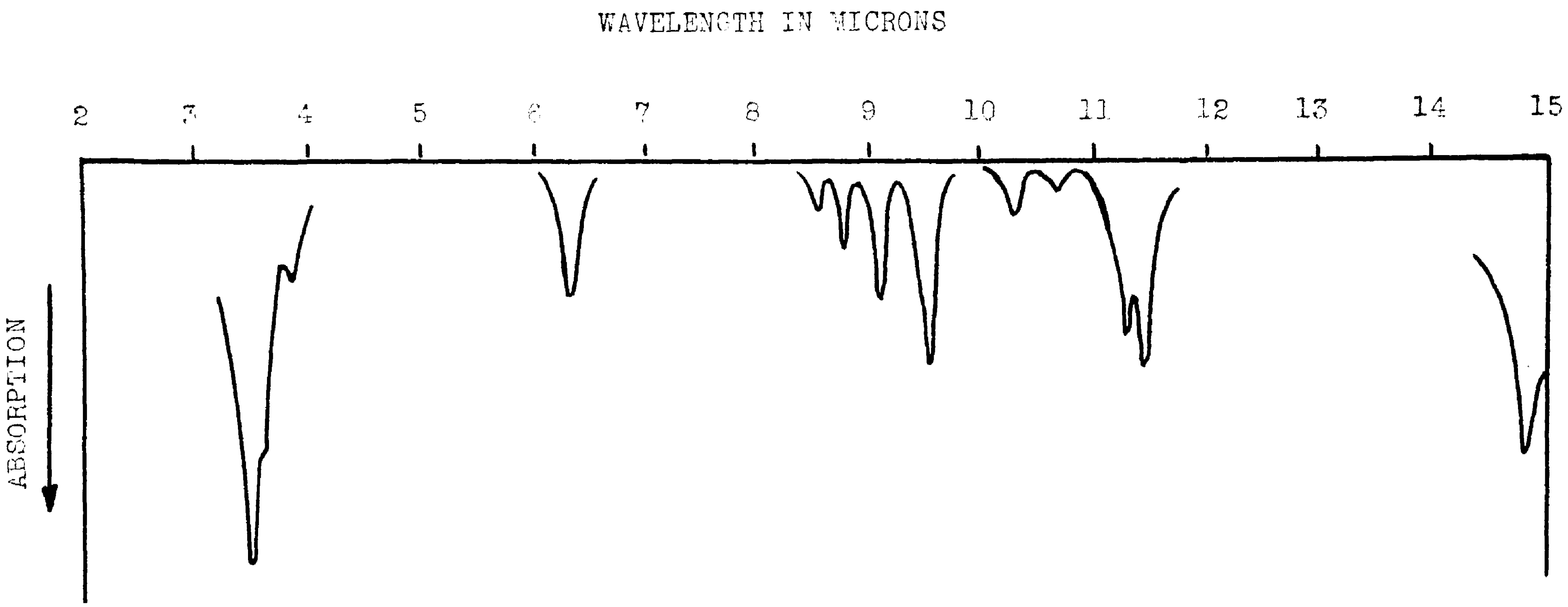


Figure 10. Infrared spectrum of methyl-lithium in Nujol mull.

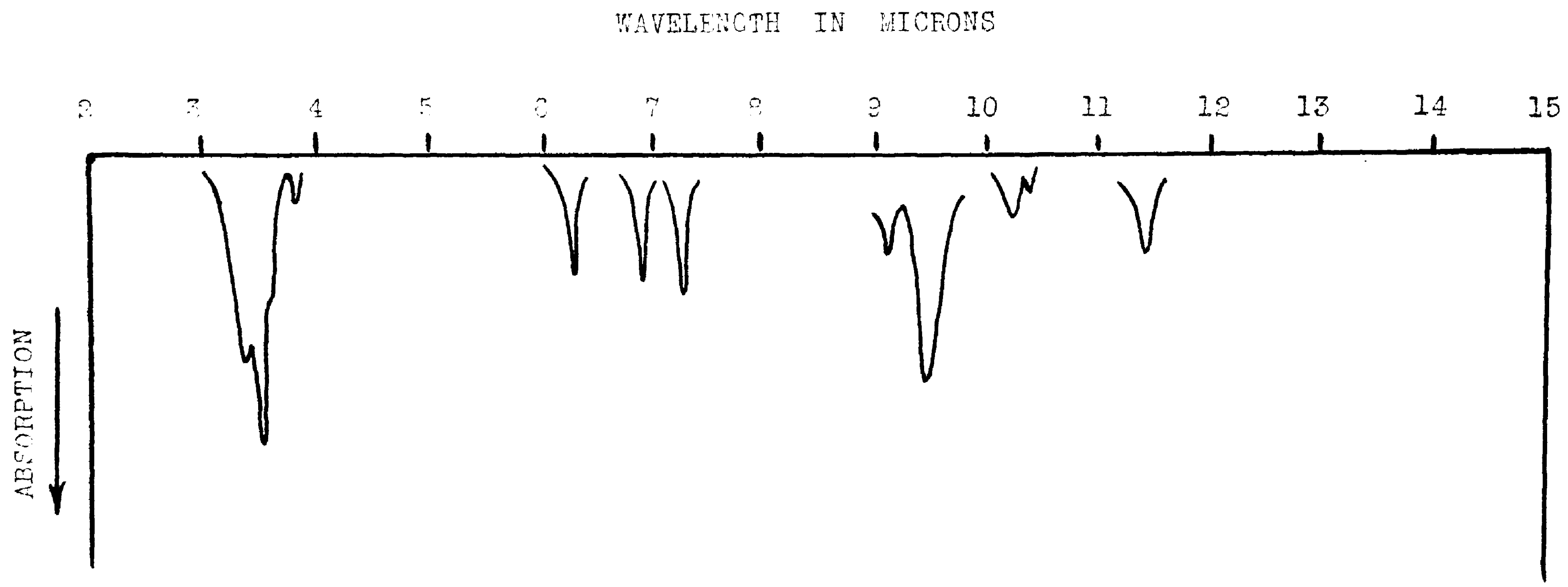


Figure 11. Infrared spectrum of methyl-lithium in perfluorokerosene mull.

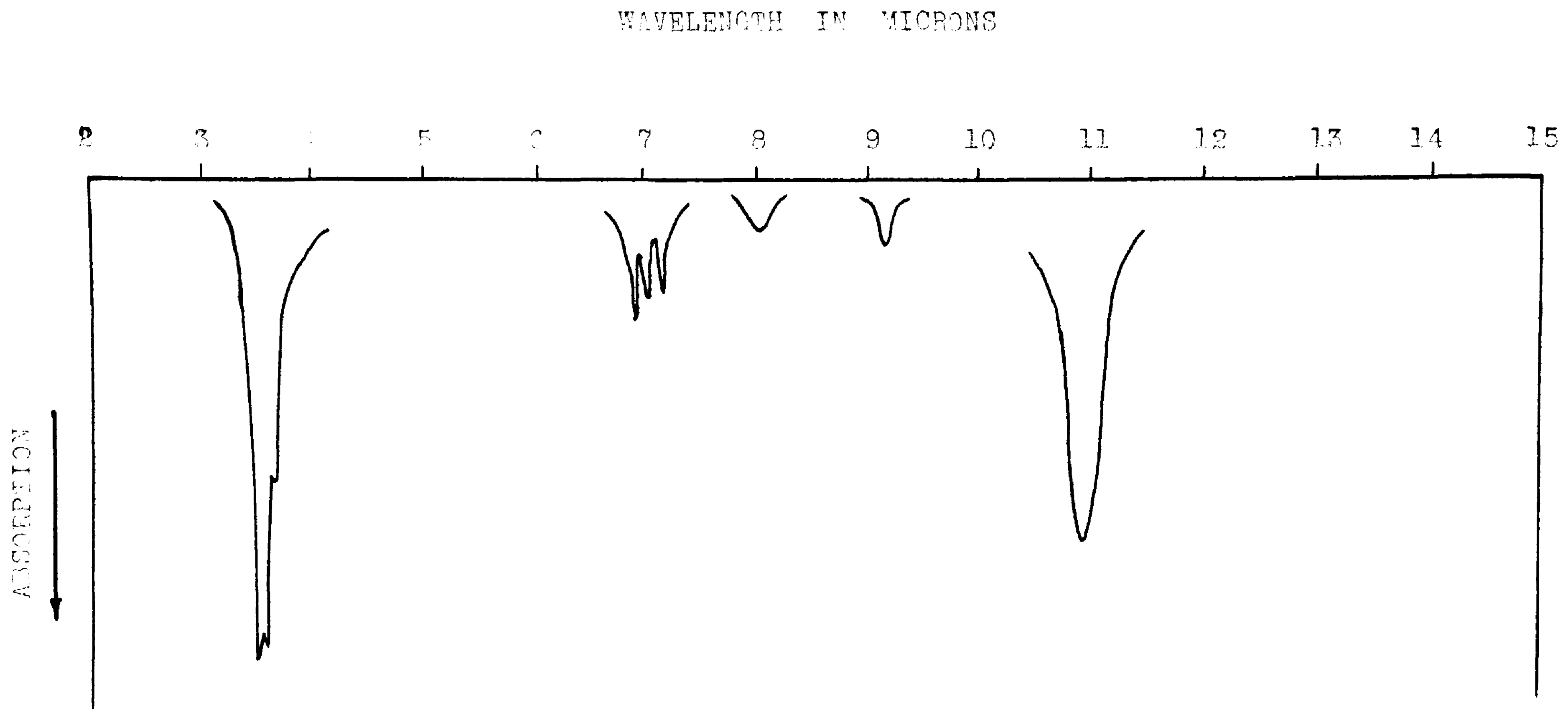


Figure 12. Infrared spectrum of ethyl-lithium in benzene solution, concentration 0.303 molal.

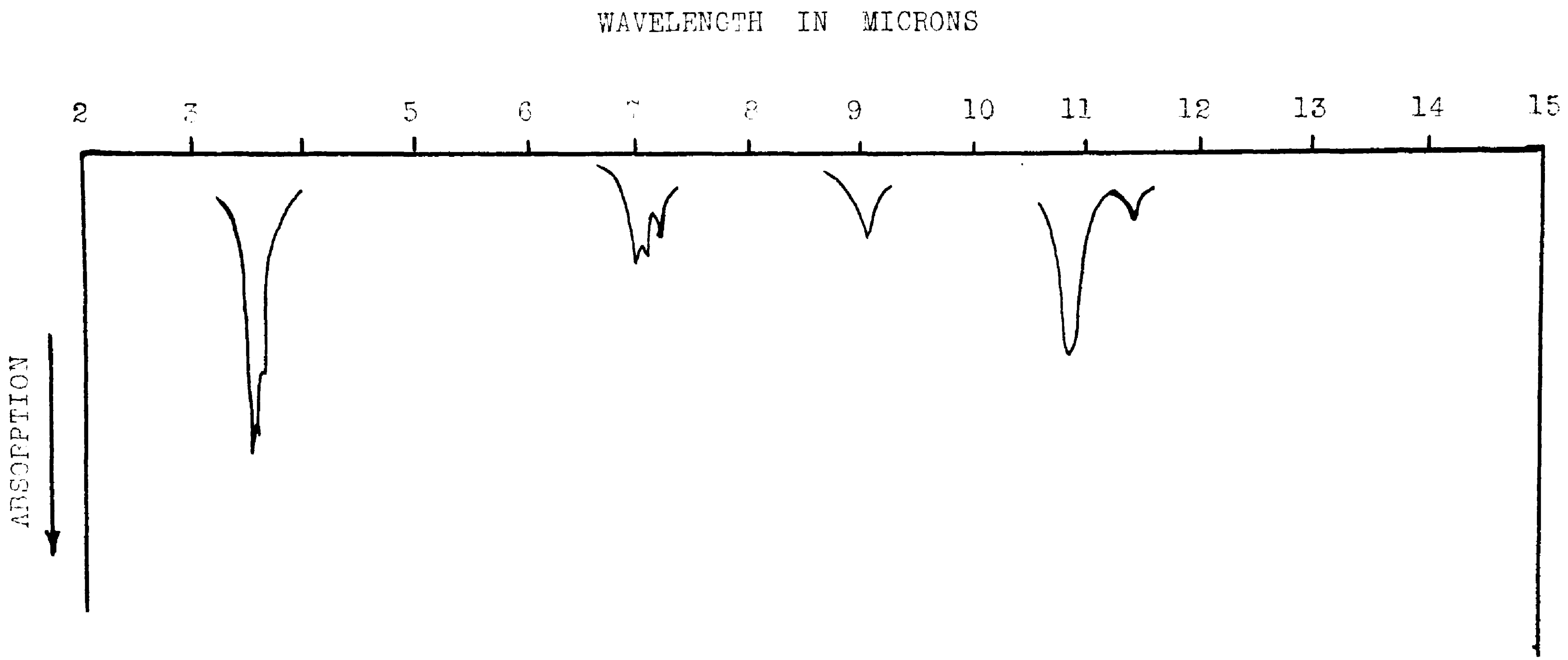


Figure 13. Infrared spectrum of ethyl-lithium in benzene solution, concentration 0.0779 molal.

TABLE VI

LIST OF FREQUENCY MAXIMA FOR METHYL-LITHIUM SPECTRA

Nujol Mull		Perfluorokerosene Mull	
Frequency (cm^{-1})	Intensity	Frequency (cm^{-1})	Intensity
—	—	2925	6
2830	10	2826	10
2718 (s)*	3	2718 (s)*	3
2596	3	2590	1
1612	3	1612	3
—	—	1442	3
—	—	1380	3
1168	1	—	—
1150	1	—	—
1105	4	1105	2
1056	8	1056	5
—	—	980	2
967	1	967 (s)*	1
930	1	—	—
897	4	—	—
883	5	880	2
672	6	—	—

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*The symbol (s) applies to bands which appear as a shoulder on the side of a more intense band.

TABLE VII

LIST OF FREQUENCY MAXIMA FOR ETHYL-LITHIUM SPECTRA

Nujol Mull		Perfluorokerosene Mull	
Frequency (cm^{-1})	Intensity	Frequency (cm^{-1})	Intensity
----	----	2925	6
----	----	2810	10
2745	6	2745	8
----	----	1478	2
----	----	1450	3
----	----	1437 (s)*	2
----	----	1386	2
1230	1	----	----
1099	2	1104	3
1052	3	1062	4
948	3	948	6
918	1	904 (s)*	5
878	5	878	8
672	10	----	----

*See Table VI.

TABLE VIII

LIST OF FREQUENCY MAXIMA FOR INFRARED SPECTRUM OF ETHYL-LITHIUM IN BENZENE SOLUTION

Frequency (cm^{-1})	Intensity
2762 (s)*	10
2730	8
1448	3
1416	2
1374	2
1239	1
1098	2
920	9
877 (s)*	2-0

*See Table VI.

TABLE II

X-RAY POWDER DIFFRACTION DATA FOR METHYL-LITHIUM

Line	θ(degrees)	d(Å)	Miller Indices	a_0(Å)	Intensity
1	5.01	8.83	100	8.83	4
2	7.04	6.29	110	8.89	9
3	8.65	5.127	111	8.88	3
4	11.22	3.956	210	8.846	3
5	12.31	3.135	211	8.853	1-2
6	14.22	3.000	220	8.866	2
7	14.89	2.8167	300,221	9.000	10
8	15.88	2.5638	310	8.9072	2
9	17.50	2.4656	222	8.8812	1
10	18.22	2.3756	320	8.8900	2
11	18.93	2.1610	321	8.8885	1
12	20.90	2.0980	410	8.9050	1
13	21.56	1.9505	411,330	8.9010	1-2
14	22.05	1.9000	331	8.9506	1-2
15	23.28	1.8658	421	8.9384	1
16	23.94	1.7802	332	8.9118	1-2
17	24.41	1.7466	422	9.1104	1-2
18	25.66	1.7150	500,430	8.9010	1
19	26.20	1.6587	510,431	8.9059	1
20	26.72	1.7150	511,333	8.9113	1
21	27.69	1.6587	520,432	8.9323	1-2
22	29.78	1.5522	522,441	8.9168	1

TABLE X

X-RAY POWDER DIFFRACTION DATA FOR ETHYL-LITHIUM

Line	θ	$\sin^2\theta^*_{obs}$	Miller Indices	$\sin^2\theta^*_{calcd.}$	Intensity
1	4.94	7.40	010	7.30	8
2	6.55	13.03	100	13.46	6
3	8.28	20.78	110	20.76	7
4	8.99	24.40	101	22.52	4
5	9.87	29.40	020	29.20	6
6	11.46	39.30	002	36.24	1-2
7	12.38	46.00	012	43.54	7
8	12.64	47.90	102	49.70	5
9	13.45	54.1	200	53.8	8
10	14.15	59.8	210	61.1	6
11	14.46	62.5	201	62.9	2
12	15.11	68.0	022	65.4	1
13	15.88	75.1	031	74.8	3
14	16.38	79.6	130	79.2	5
			122	78.9	
15	17.66	92.1	221	92.1	4
16	18.40	99.6	212	97.3	1
			032	101.8	
17	19.53	111.7	023	110.7	1-2
18	19.98	116.7	040	116.6	2
			132	115.4	
19	21.98	140.1	141	139.4	4
20	22.37	144.6	004	144.8	2
21	23.51	159.2	104	158.3	4
			321	159.2	
22	24.28	168.6	142	166.5	1
			114	165.6	
23	25.29	182.5	050	182.5	1
24	26.47	198.3	204	198.6	1
			043	198.3	
25	27.65	215.4	400	215.5	4
26	28.52	227.8	224	227.8	1-2
27	29.24	238.6	340	237.7	1
			250	236.3	
28	30.42	256.0	421	253.8	1
			412	259.0	
29	31.42	271.2	252	272.5	1
30	37.71	374.0	521	373.9	1-2
31	39.02	396.0	522	401.0	1-2

*All $\sin^2\theta$ values x 10^{-3}

The angles corresponding to the distances measured on the single-crystal rotation films between layer lines of the same index but opposite sign are listed in Table XI.

Microscopic Examinations

It has been mentioned that the ethyl-lithium crystals tend to grow as flat plates. When viewed under the microscope with the flat sides horizontal they are transparent to white light. Under crossed Nicols with a white light source the crystals appear colorless except for occasional polarization colors. The crystals do not extinguish when rotated under crossed Nicols through 360°. When viewed with sodium light under crossed Nicols the crystals are bright except for patches of dark; they again fail to extinguish under rotation. Very thin sections around the edge of the crystals do show extinction every 90°; the orientation of the crystals with respect to the plane of polarization when this occurs was noted for use in aligning the crystals on the goniometer for exposure to x-rays.

When the crystals are viewed with the flat sides vertical they do show extinction every 90°, both with white and sodium light. The extinction occurs when the plane of the flat faces is parallel or normal to the plane of polarization. Although many orientations of the crystals were examined, none were found in which the crystals appeared isotropic.

The crystals of methyl-lithium, when viewed under crossed Nicols, appeared to be isotropic. On exposure to the atmosphere for a short

TABLE XI

LAYER-LINE SPACINGS FROM SINGLE-CRYSTAL ROTATION PHOTOGRAPHS OF ETHYL-LITHIUM

Orientation	Layer Line	θ	Sin θ	d (Å)
1	2	12° 32'	0.216	7.15
1	4	25° 27'	0.420	7.35
2	1	9° 57'	0.164	9.40
3	2	10° 42'	0.189	4.07

time, while still covered with a little oil, they were transformed into an anisotropic material, presumably lithium hydroxide. From the fact that no anisotropic material was present in the preparation when first viewed it may be inferred that the material was essentially free of lithium hydroxide.

Benzene Solutions of Ethyl-lithium

The data obtained from density, dielectric constant and freezing point depression measurements on benzene solutions of ethyl-lithium are summarized in Tables XII-XIV.

TABLE XII

DIELECTRIC CONSTANTS OF SOLUTIONS OF ETHYL-LITHIUM IN BENZENE AT 25°C.

Contents of Cell	Capacitance Reading at Balance Point	ε
Air	1003.04	2.274
Benzene	895.56	
Ethyl-lithium Solutions:		
Air	1002.84	2.2816
0.0779 molal	894.68	
Air	1003.02	2.2889
0.249 molal	894.28	
Air	1003.08	2.2949
0.347 molal	893.84	

TABLE XIII

DATA FROM USE OF PYCNOMETER IN DENSITY DETERMINATIONS

Contents of Pycnometer	Reading on Calibration Marks (ml.)	Weight (gms.)
Air	----	44.9640
Water	0.026	66.0050
Benzene	0.016	63.3790
Ethyl-lithium Solutions:		
0.261 molar	0.020	63.3366
0.0736 molar	-0.035	63.2967
0.0236 molar	0.038	63.4138

TABLE XIV

DATA FROM FREEZING-POINT LOWERING EXPERIMENTS ON BENZENE SOLUTIONS OF ETHYL-LITHIUM

Concentration (molal)	$-\Delta T$ (°C.)	$\bar{n}$
0.303	0.280	5.32
0.392	0.352	5.71
0.347	0.267	6.65
0.0779	0.063	6.09
0.249	0.184	6.94

CALCULATIONS AND INTERPRETATIONS OF RESULTS

X-ray Diffraction Data

From the isotropic behavior of methyl-lithium crystals when viewed under crossed Nicols it may be inferred that they are of cubic symmetry. By proceeding on this assumption it is a relatively simple matter to assign the correct indices to the reflections on the powder pattern. The interplanar spacing, d, corresponding to any given reflection on the pattern is obtained from the Bragg relation, $d = \lambda/2\sin\theta$. This value of d is related to the unit cell dimension a_0 by the relation $a_0 = d\sqrt{h^2 + k^2 + l^2}$ where h, k and l are the Miller indices of the plane giving rise to the reflection (32). In Table IX the values of a_0 are listed for each line on the powder pattern along with the Miller indices assigned to that line.

From these values of a_0 an average value for the unit cell dimension, $a_0 = 8.909 \pm 0.016$ Å, is obtained. If it is assumed that there are 16 molecules per unit cell a value for the density of methyl-lithium of 0.826 gm./cm.^{3} is obtained, in good agreement with the observation that the crystals have about the same density as a solution consisting of about 80% benzene (density 0.89 gm./cm.^{3}) and 20% pentane (density 0.63 gm./cm.^{3}).

In order to determine the space group to which the crystal structure may be assigned it is necessary to determine the systematic absences, if any, among the reflections. Inspection of the list of indices in

Table IX reveals that the only systematic absences present are the h00 reflections where h is even. Now it can be shown that this systematic absence cannot be the result of any of the symmetry elements which usually produce absences, such as screw axes or glide planes (32). It must be concluded that these reflections are absent because they have such a low intensity that they are not visible on the film, or because the particular arrangement of the atoms in the crystal, exclusive of the symmetry elements mentioned above, leads to their having zero intensity.

Since there are no systematic absences the lattice type must be primitive as opposed to face- or body-centered. Inspection of the symmetry properties of all the primitive lattice types belonging to the cubic system reveals that there are five which are without systematic absences; these five are P23, Pm3, P432, P$\bar{4}$3m and Pm3m (34). In order to determine which of these five space groups to assign to the methyl-lithium crystals it is necessary to have more information. Space groups P23 and P432 are enantiomorphous; that is, the crystals which have this space group symmetry are either right or left-handed. If a crystal exhibits optical activity when viewed under crossed Nicols it almost surely belongs to one of the enantiomorphous classes, but the corollary of this statement is not true--many crystals which are enantiomorphous do not show observable optical activity. The methyl-lithium crystals do not show observable optical activity, and thus cannot be assigned on this basis to any one of the above five space groups, nor can they be excluded from any.

When the space group cannot be unambiguously assigned as in the present case it is usually necessary to proceed with a structural analysis, comparing the observed intensities with calculated values based on trial structures involving the possible space groups. Since it is not possible to obtain sufficient information from the intensities of the reflections from powder patterns, no further progress can be made in the present work toward determining the crystal structure of methyl-lithium.

The behavior of ethyl-lithium crystal under the polarizing microscope was of considerable help in analyzing the x-ray data. The failure of the crystals to extinguish when rotated under crossed Nicols is evidence of optical activity. This property limits the number of possible symmetry groups to those which are enantiomorphous-those which lack planes of symmetry, inversion axes and a center of symmetry. From the fact that the crystals exhibit anisotropic behavior in all orientations it may be inferred that the symmetry which they possess is of a lower order than that possessed by the tetragonal system, since for this class there is one orientation which exhibits isotropic behavior.

Single-crystal rotation photographs were taken of the material in three mutually perpendicular orientations which coincided with the positions of extinction observed under the microscope. These photographs exhibited reflection spots which were symmetrically arranged about the center of the picture, indicating that the lattice possessed mutually perpendicular crystal axes. This evidence, in combination with the results of microscopic observation, fixed the crystal system as orthorhombic. This assignment is in agreement with the fact that there are three different layer-line spacings. From these spacings the unit cell dimensions $a_o = 7.25$, $b_o = 9.40$ and $c_o = 4.07$ Å are calculated.

For the purpose of indexing an orthorhombic powder pattern an expression of the form

$$\sin^2\theta = Ah^2 + Bk^2 + Cl^2$$

is best used (31). The constants A, B and C are defined by the relations,

$$A = \left(\frac{\lambda}{2a_o}\right)^2 \qquad B = \left(\frac{\lambda}{2b_o}\right)^2 \qquad C = \left(\frac{\lambda}{2c_o}\right)^2$$

Using the values for the unit cell dimensions obtained from the layer line spacings, provisional values of A, B and C may be determined. These values may then be used to calculate values of $\sin^2\theta$ for all reflections through about the fifth order. By comparing these calculated values with the observed values (Table X), an assignment of indices can be made for most of the reflections on the powder pattern. Since the values of $\sin^2\theta$ for the larger angle reflections from the powder patterns are the most precise source of data, more accurate values of the unit cell dimensions are obtainable once the correct indices for these reflections have been determined. By proceeding in this manner the unit cell dimensions for the ethyl-lithium crystal were determined to be

$$a_o = 6.65 \text{ Å} \qquad b_o = 9.03 \text{ Å} \qquad c_o = 8.10 \text{ Å}$$

More accurate values of $\sin^2\theta$ for all the reflections were then calculated. These are compared with the observed values in Table X. It will be noted that in some cases there is some ambiguity in the assignment of indices to a reflection, especially among those with larger values of $\sin^2\theta$. This is the inevitable result of reflections with higher indices having the same, or nearly the same, value of $\sin^2\theta$.

Inspection of the indices listed in Table X shows that the only systematic absences are the $00l$ reflections, with l odd. This is evidence of a two-fold screw axis as an element of symmetry. As in the case of methyl-lithium, the fact that other systematic absences are not present is evidence that the lattice is primitive.

From the optically active behavior of the crystals a further restriction on the number of possible space groups may be imposed. Only those space groups with the general symmetry symbol P222 in the orthorhombic system are enantiomorphous. From the systematic absences noted above it may be deduced that the correct space group is $P222_1$.

If the number of molecules per unit cell is assumed to be 8, a value of 0.98 gm./cm.^{3} is obtained for the density, in agreement with the observation that the crystals appear to be denser than benzene (density 0.89 gm./cm.^{3}).

The largest number of equivalent positions per unit cell for the $P222_1$ space group is 4. There are thus at least two molecules per equivalent position. Since there are three diffracting atoms per molecule (the diffracting power of the hydrogens is so small it may be neglected), the positions of six atoms are required in order to determine the equivalent position completely. The single crystal rotation photographs obtained with the available equipment were not of sufficiently good quality to permit measurements of intensity on a scale necessary for a structural analysis. Also, not enough reflections were observed. It is not possible, therefore, to determine the locations of the atoms in the crystal lattice from the data secured in the present work.

Benzene Solutions of Ethyl-lithium

Densities — The densities of pure benzene and of the three ethyl-lithium solutions were calculated from the data of Table XIII; corrections for air buoyancy were made using an atmospheric pressure of 740 mm., 50% humidity, and a temperature of 25°C. The resulting values of density for benzene and the three solutions are plotted in Figure 14 against the molal concentration.

Freezing-Point Lowerings — Using a value of 5.12 for the molal freezing-point depression constant of benzene, the magnitude of the freezing-point depression for a non-associated solute present in molal concentration $\bar{m}$ should be $\bar{m} \times 5.12$ degrees. This number divided by the observed freezing-point lowering for the solution may be taken as the average degree of association, $\bar{n}$. Values of $\bar{n}$ are listed in Table XIV for the solutions which were measured. Although the use of the constant 5.12 as independent of concentration is an approximation, the error introduced by its use is small compared with the uncertainty in the measurements.

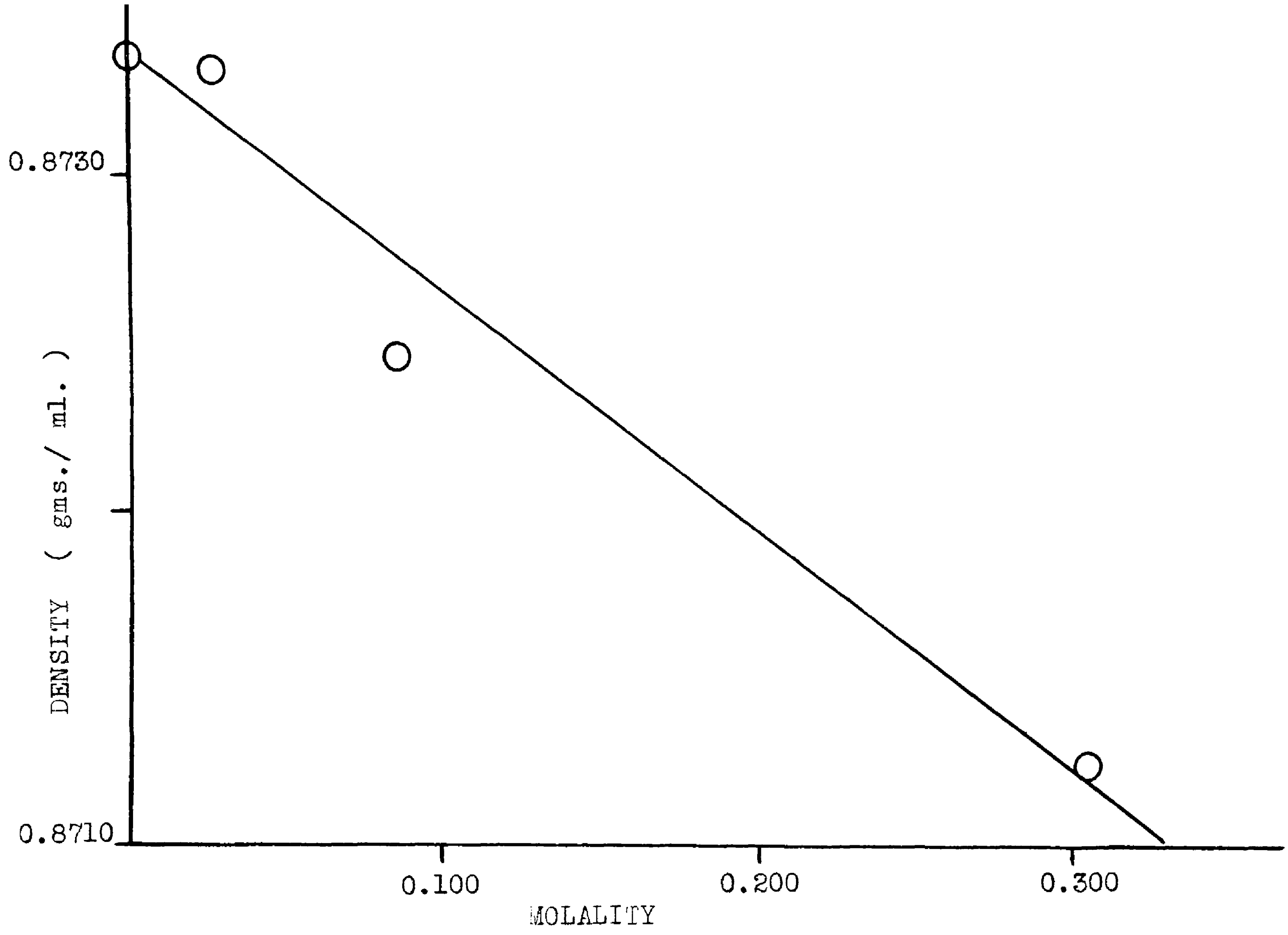

Figure 14. Density *vs*. molality for ethyl-lithium solutions in benzene.

Dielectric Constant -- Figure 15 is a graph of mole fraction of solute, N_2, vs. the difference between the readings of the standard capacitor, S, for the cell in air and when filled with solution or pure benzene. It is seen that the points define an approximately linear curve. The value of the dielectric constant of air may be taken as 1.000 and that of pure benzene as 2.274; the difference between the capacitor readings for these two materials is 107.48. From this the value of $d\,\mathcal{E}/dS$ is 0.01185. Using this value the dielectric constant of a solution of mole fraction N_2 may be determined by noting the difference between the value of S at mole fraction N_2 and the extrapolated value of S at $N_2 = 0$. This difference is multiplied by 0.01186 and added to 2.274 to give the dielectric constant of the solution.

The molar polarization of a solution, P_{12}, may be expressed as

$$P_{12} = \left(\frac{\mathcal{E}_{12} - 1}{\mathcal{E}_{12} + 2}\right)\left(\frac{N_1M_1 + N_2M_2}{d}\right)$$

where N_1 and N_2 are the mole fractions of solvent and solute in the solution, M_1 and M_2 are the respective molecular weights, and d the density of the solution (35). From the relation

$$P_{12} = N_1P_1 + N_2P_2$$

where P_1 and P_2 are the molar polarization of solvent and solute, P_2 may be calculated when P_1 is known.

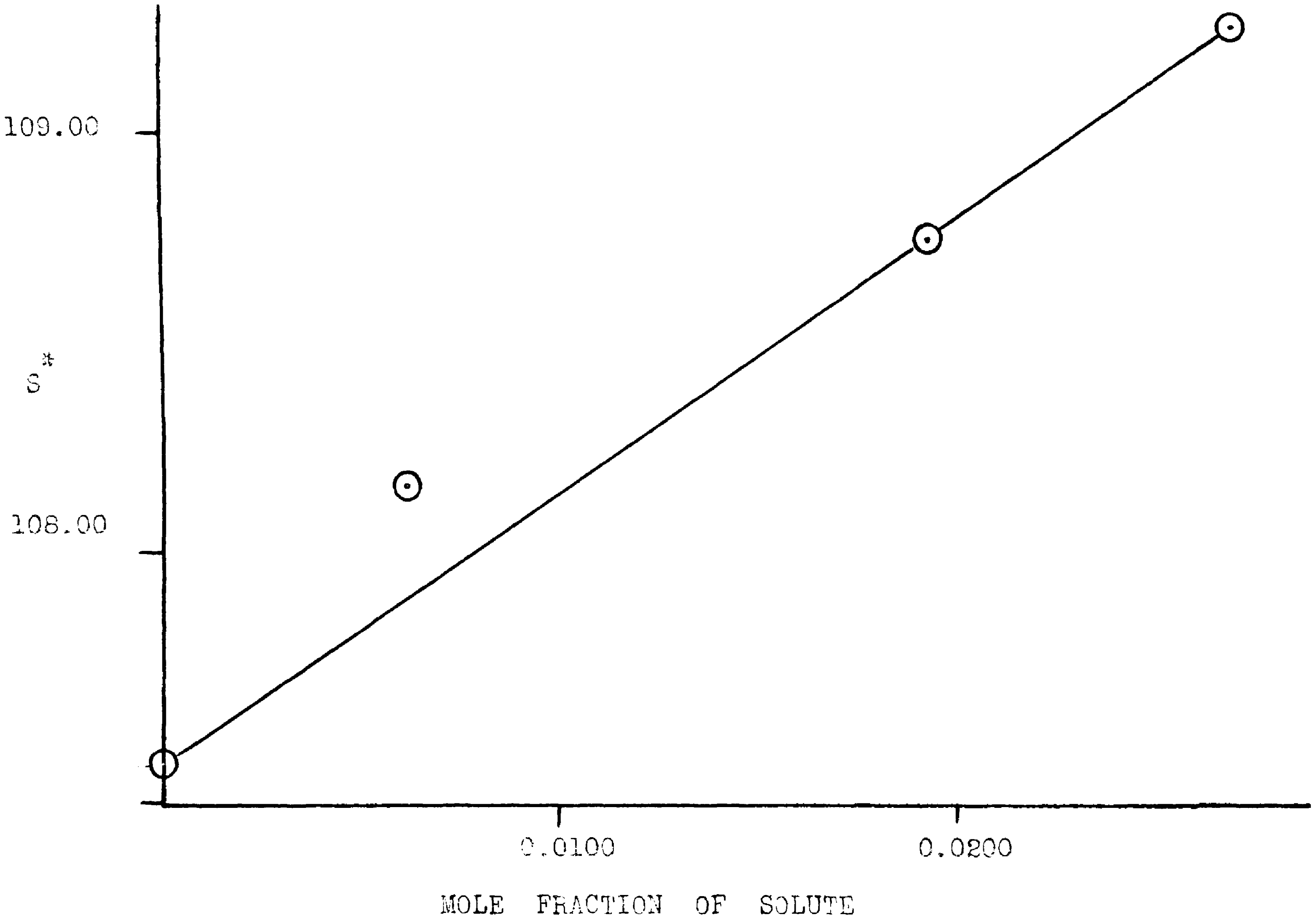

Figure 15. Graph of standard capacitor readings *vs.* mole fraction of solute for solutions of ethyl-lithium in benzene.

* see text.

The molar polarization of ethyl-lithium calculated in this way from the results listed above is 26.8 cm.^{3}.

The total molar polarization of a compound may be considered to be the sum of three separate polarization effects, the orientation polarization, P_o, the electronic polarization, P_e, and the atomic polarization, P_a. P_o is the result of a permanent electric moment within the molecule, P_e is the result of distortion of the electron distribution in the molecule under the influence of an applied field, and P_a arises through the formation of an induced moment because of changes in nuclear position under the influence of a field. The magnitude of P_e is determined by measurement of the dielectric constant of the material at visible light frequencies; the period of the orientation and atomic polarizations is too long for them to contribute to the total polarization at these frequencies. The atomic polarization is difficult to evaluate; it is small in comparison with the orientation effects in most cases and is usually ignored or taken as 10-20% of P_e. When it is not possible to obtain reliable values of dielectric constant at optical frequencies it is possible to estimate P_e by use of additive values of atomic refraction for each atom in the molecule. The value of P_e for ethyl-lithium estimated in this way is about 11.5, using a value of 1.2 for the atomic refraction of lithium. The sum of atomic and orientation polarizations is then 26.8-11.5 = 15.3 cm.^{3}.

From the Clausius-Mosotti relation the expression

$$\mu = 0.0128 \sqrt{P_o T}$$

where μ is the dipole moment of the molecule in Debyes, and T is the absolute temperature, may be derived (35). If the value of 15.3 cm.^{3} obtained above is assumed to be due entirely to orientation polarization a value of 0.86 Debye is obtained for the electric moment of ethyllithium in benzene.

DISCUSSION

Infrared Spectra

In analyzing an infrared spectrum which has been observed for the first time it is frequently helpful to compare it with the spectra of compounds which bear some similarities to the compound being investigated. In doing this in the present case frequent reference will be made to the volume by L. J. Bellamy (36) and to the Landolt-Börnstein compilation (37).

The frequencies which are characteristic of the C-H stretching vibrations in alkyl groups occur in the region 3000-2850 cm^{-1}, with some hydrocarbons absorbing in the region 2850-2500 cm^{-1} (36). The vibrations which occur in this region for methyl- and ethyl-lithium are assignable to this class of vibrations. In observing this region of the spectrum with an instrument which utilizes a sodium chloride prism it is not possible to detect small differences in frequency with any accuracy because of the low dispersion of sodium chloride in this region. It does appear, however, that the C-H frequencies observed for the lithium alkyls are somewhat lower than usual; the bands occurring at about 2730 cm^{-1} in both methyl- and ethyl-lithium and the band which occurs at 2590 cm^{-1} in methyl-lithium are unusually low in frequency. It is noteworthy that a weak absorption at 2677 cm^{-1} has been observed in the spectrum of trimethylaluminum dimer vapor (15). Bellamy remarks that although a number of hydrocarbons absorb in this region the intensity is very weak. Cyclic compounds such as dioxan, tetrahydrofuran and cyclohexanone have somewhat stronger bands in this region. Examination of the spectra of a number of small-ring compounds such as cyclopropane and cyclobutane derivatives (38) shows that they also show absorption in the region 2800-2500 cm^{-1}. It is quite possible that the absorptions observed in this region for the lithium alkyls are due to the presence of rings such as those discussed in the introduction, formed through electron-deficient bonding. It is significant that metal alkyls such as the zinc, cadmium, mercury or tin methyls do not absorb in the region in question.

Absorptions in the region 1480-1375 cm.$^{-1}$ are associated with deformation vibrations of the C-H linkages in CH_3- and -CH_2- groups. The one band at 1442 cm.$^{-1}$ in methyl-lithium and the three bands in the region 1480-1435 cm.$^{-1}$ in ethyl-lithium may be assigned to the asymmetrical hydrogen bending mode, while those in the vicinity of 1380 cm.$^{-1}$ are assignable to the symmetrical mode. The assignment which is proper to the band which occurs at 1612 cm.$^{-1}$ in methyl-lithium is not known. It does not seem likely that it could be due to a C-H deformation mode; it is true, however, that the C-H deformations in strained ring systems tend to occur at higher frequencies than usual.

It is not possible to assign the absorptions which occur in the spectral range 1250-900 cm.$^{-1}$ to particular vibrations. In general these are associated with skeletal vibrations of carbon chains and of ring systems. Since the arrangement of bonds in the crystalline lithium alkyls is not known it can only be said here that these bands may be the result of skeletal vibrations involving ring structures.

It appears that the band occurring at about 880 cm.$^{-1}$ is due to the stretch vibration of the metal-carbon bond. It is present in all the spectra of both methyl- and ethyl-lithium with moderate to strong intensity. The vibration does not appear to be very sensitive to mass changes, since the frequency is about the same for the two compounds.

There is a relatively large increase of 42 cm.$^{-1}$ in the frequency of this vibration for ethyl-lithium in benzene solution as compared with the solid. In dilute solution, however, a band at 878 cm.$^{-1}$ is evident as a low intensity absorption. Since ethyl-lithium is associated in benzene solution, as evidenced by the freezing-point depression results, it seems reasonable to suppose that the band at 920 cm.$^{-1}$ is due to Li-C bonds which are involved in association, that at 878 cm.$^{-1}$ to the unassociated material. Further indication that this is the case is provided by the fact that in the more dilute solutions the peak at 878 cm.$^{-1}$ appears to grow relatively more intense in comparison with the one at 920 cm.$^{-1}$ as the concentration is decreased. This is what one would expect if an equilibrium existed between associated and unassociated species. If it were possible to examine more dilute solutions this point could be tested more thoroughly, but in order to do this it would be necessary to employ longer path lengths of solution; since benzene absorbs rather strongly in this region the transmission of radiation through the cell would be unacceptably low.

It is perhaps significant that the peak at 920 cm.$^{-1}$ is of relatively narrow bandwidth. In the case of alcohols, association through intermolecular hydrogen bonding results in a broad absorption band due to the stretching vibrations of associated O-H bonds. The broad shape of the associated band is usually attributed to the fact that the alcohol associates into various polymeric forms in which the molecules are involved in bridge bonding to different extents, so that the broad band observed is a composite of a number of sharper bands. The narrow width of the band due to associated material in the case of ethyl-lithium indicates that the association is not the result of a more or less random dipole-dipole clustering, but involves the formation of bonds of definite energy. This is also indicated by the large difference in frequency between associated and non-associated bands; a shift of this magnitude points to a marked change in the lithium-carbon bond on association.

If the absorption at 878 cm.$^{-1}$ is assumed to be due to Li-C stretching in monomeric ethyl-lithium molecules, and if a harmonic oscillator approximation is made, it is possible to estimate the magnitude of the force constant for the vibration. The frequency of a harmonic oscillator is related to the force constant and the vibrating mass by the expression,

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

In calculating k for the Li-C stretch the vibration is assumed to involve a motion of the lithium atom as one end of the oscillator and the alkyl radical, $-C_2H_5$, as the other; the value of the reduced mass for this system, 5.59 gms./mole, is used in the above expression. The value of k calculated in this way for ethyl-lithium is about 2.5 x 10^5 dynes/cm.

This value is only a rough approximation; the assumption of harmonicity is not likely to cause a very large error, but the value which should be chosen for the reduced mass is open to question. For lack of more information on the state of the molecule, the assumption made above seems to be the best; if the resulting value for the force constant is in error it is probably low.

It is of interest to compare the calculated value of k for the Li-C stretch with that of other bonds to carbon. The values of k x 10^5 dynes/cm. for the halogen bonds are 3.4, 2.9 and 2.3 for C-Cl, C-Br and C-I, respectively (38). It is seen that the value of 2.5 for the Li-C bond is of about the same magnitude as the values of the carbon-halogens.

Braude (8) has remarked that the bond energy of the carbon-lithium bond must be of the same general magnitude as that of carbon-chlorine. The dissociation energies of the carbon-halogen bonds in ethyl halides are listed below for comparison with the force constants (37).

C_2H_5-Cl	88 kcal./mole
C_2H_5-Br	69 kcal./mole
C_2H_5-I	54 kcal./mole

It is seen that there is a parallel relation between the magnitude of the force constant and the bond energy; this is shown in Figure 16.

If this relation were to hold for the carbon-lithium bond the bond energy would be about 60 kcal./mole.

It is difficult to account for the strong band which appears at 672 cm.$^{-1}$ for Nujol mulls of both methyl- and ethyl-lithium. It is

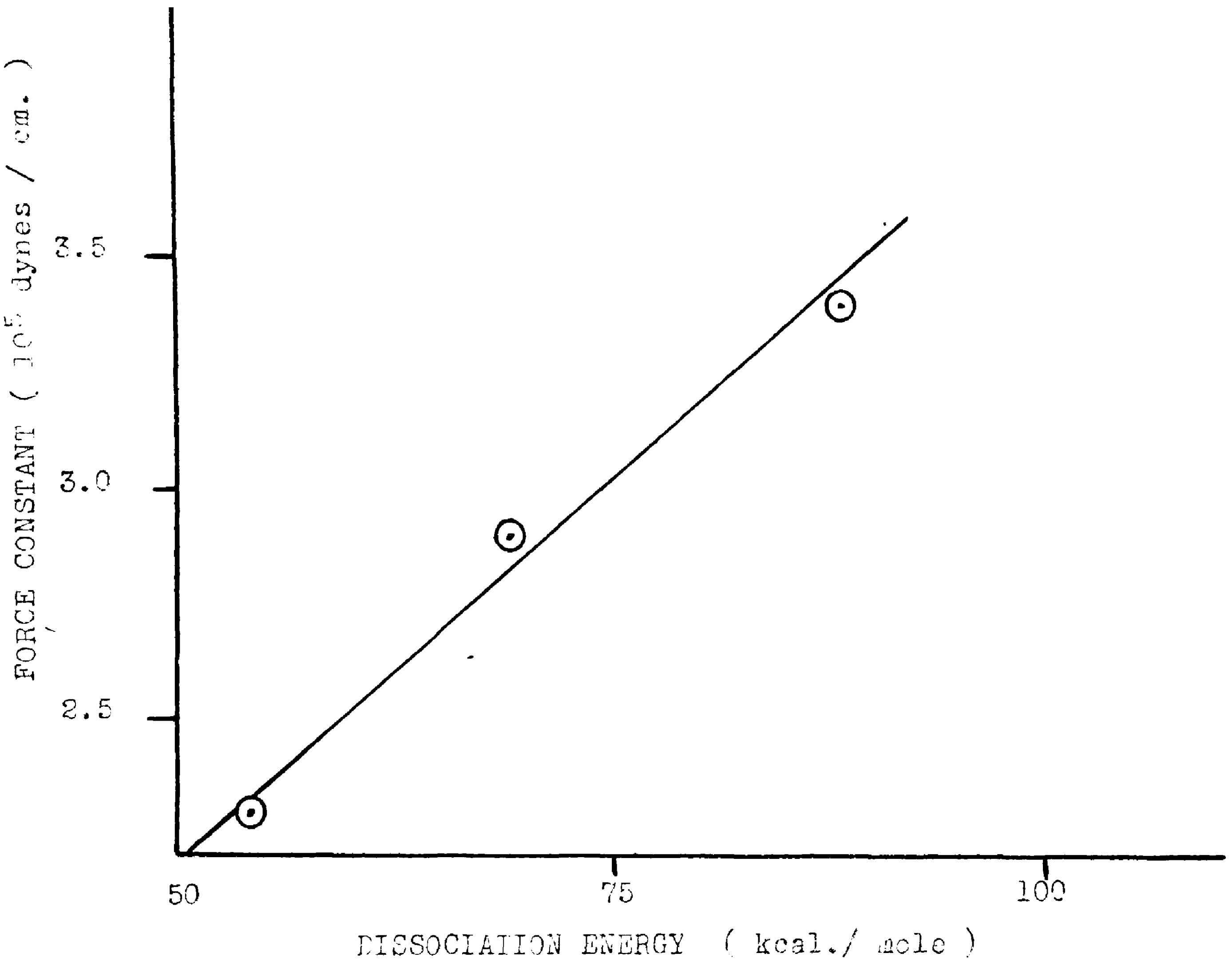

Figure 16. Graph of dissociation energy *vs*. force constant for carbon - halogen bonds.

certain that this band is not present in the spectra of benzene solutions of ethyl-lithium; because perfluorokerosene absorbs quite heavily in this region it is not possible to determine with certainty whether there is any absorption due to the compounds when used with this mulling agent. There is no evidence of reaction when the mulls with Nujol are made up, but the possibility exists that the band is due to reaction of the lithium alkyls with some material in the mulling agent which results in a product which absorbs in this region.

Although strong, narrow bands are not common in this spectral range, there are some materials which do show characteristic absorptions; the C-H bending mode of acetylenic carbons falls in the range 600-700 cm.$^{-1}$, and cyclohexene has been observed to show a strong narrow absorption maximum at 675 cm.$^{-1}$. If the band really is due to the lithium alkyls, its absence in the spectra of ethyl-lithium solutions in benzene may be due to the fact that it is produced by vibrations of bonds which are broken on solution of the crystal material. In this connection, however, it should be said that some preliminary work which was done on the spectra of ethyl-lithium in pentane showed the presence of a band at 672 cm.$^{-1}$.

Benzene Solutions of Ethyl-lithium

Although the uncertainty in the average degree of association as measured by freezing-point depression is quite large, the data make one point strikingly clear—ethyl-lithium is highly associated in benzene solution. From the viewpoint of molecular structure theory it is of importance to determine the nature of this association and the resulting configuration. In the preceding section a value of 15.3 cm.^{3} was obtained for the sum of the atomic and orientation polarizations. If the atomic polarization is taken to be zero a value of 0.86 Debye for the electric moment of each monomeric molecule follows. Since the material is associated to the extent of about six-fold, however, it is apparent that the entities which give rise to the observed polarization must have much larger moments than this. For example, if it is assumed that the ethyl-lithium exists entirely as a hexamer, then the moment of each hexameric molecule would be approximately 2.1 Debye. It is not unlikely, however, that an appreciable fraction of the observed polarization is due to atomic polarization. Davidson and Sutton have related the magnitude of the atomic polarization to the presence of low frequency vibrations in the molecule which produce a change in electric moment (39). These low frequency vibrations are usually associated with the bending modes of bonds. In the case of ethyl-lithium the Li-C bond probably has a low frequency bending mode with a relatively small bending force constant, and this vibration will give rise to a contribution to the atomic polarization. In addition to this the configuration which is formed through association will have associated with it some low energy deformation frequencies, so the atomic polarization for the configuration will be greater than the sum of the atomic polarizations of the individual ethyl-lithium molecules. If the frequencies of these lower energy vibrations were known from spectral studies in this region it would be possible to estimate P_a, but this information is not available.

Diethylmercury (40) in benzene solution has an atomic polarization of 3.19 cm.^{3}. The value of the atomic polarization of monomeric ethyl-lithium must surely be much less than this. If ethyl-lithium is assumed to be hexameric in the solutions, the total molar polarization for the hexamer is about 160 cm.^{3}. The electronic polarization would be about 70 cm.^{3}, leaving a value of about 90 cm.^{3} for the sum of atomic and orientation polarizations. It does not seem possible that such a large polarization can be due entirely to atomic polarization, so that the supposed hexamer would have to possess a permanent electric dipole of magnitude less than 2.1 Debye. The infrared spectra show that in the concentration range in which dielectric constant data were obtained the ethyl-lithium molecules exist almost entirely as associated species, and since the freezing-point depression results indicate an average degree of association of six, the example of hexamer formation which was used above must represent the actual situation to a fair extent.

If it is assumed that a hexamer is formed, and that the bonds which are used in forming the hexamer do not contribute largely to the atomic polarization of the polymer, a rough estimate of the value of the upper limit of the atomic polarization of such a configuration may be attempted. P_a for diethylmercury is 3.19 cm.^{3}; the value for the monomeric ethyl-lithium is probably less than half this, since there is only one metal-carbon bond in the lithium compound, and the frequencies of corresponding vibrations are higher. A value of 1.5 cm.^{3} may be taken as an upper limit; since there are six molecules in the supposed hexamer the sum of atomic polarizations due to the individual molecules is about 10 cm.^{3}. In addition to this polarization, however, the possibility of contributions to the atomic polarization from low frequency skeletal vibrations of the hexameric configuration exists. Beryllium acetylacetonate (41), which contains two six-membered, non-planar rings possesses an atomic polarization of about 25 cm.^{3}. If this value is taken as an upper limit for the contribution which the skeletal modes of the ethyl-lithium polymer make to the atomic polarization the total polarization is then 35 cm.^{3}. This leaves about 55 cm.^{3} for the value of the orientation polarization, corresponding to an electric moment for the hexamer of 1.6 Debye.

There are undoubtedly many possible ways in which the ethyl-lithium molecules can be arranged in hexameric configurations which possess a permanent dipole of about 1.6 Debye. Without more detailed information, however, as to the nature of the bonding, bond distances and bond angles, nothing further can be said in this regard.

PART II

THE INTEGRATED INTENSITY OF THE INFRARED ABSORPTION BAND DUE TO O-H STRETCHING IN ALIPHATIC ALCOHOLS

II. THE INTEGRATED INTENSITY OF THE INFRARED ABSORPTION BAND DUE TO O-H STRETCHING IN ALIPHATIC ALCOHOLS

By

Theodore L. Brown

AN ABSTRACT

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DOCTOR OF PHILOSOPHY

Department of Chemistry

Year 1956

Approved ______________________________

ABSTRACT

The integrated intensity of the infrared absorption band due to O-H stretching has been measured for a number of aliphatic alcohols. The change in electric moment which gives rise to the absorption is considered to be the result of a change in the degree of ionic character of the O-H bond with changing bond distance. The intensity of the band is greatest when the group attached to the hydroxyl is most electron-withdrawing. The range of intensity values is large, so that the measurement provides a sensitive measure of inductive effects. It is concluded from the results which were obtained that the sign of the first derivative of the bond moment with respect to the internuclear distance, $\frac{\partial \mu}{\partial r}$, is positive.

THEORY

The absorption of incident electromagnetic radiation by a molecule may occur as a result of a variety of energy changes within the molecule. Within a relatively narrow region of the spectrum extending from about two to twenty-five microns wavelength, part of the so-called infrared region, most molecules show absorption of certain wavelength radiations. The energy change which the molecule undergoes in this instance is associated with a vibrational motion of the constituent atoms relative to one another. Rotational motion is also involved in considering the absorption spectra of gases, but for molecules in a liquid medium the rotational components are not present. Since the work to be discussed here involves only compounds in solution, rotational spectra will not be discussed.

For purposes of analysing the observed spectra it is convenient to consider the molecule as analogous to a mechanical system consisting of point masses connected to one another by springs which correspond to the bonding forces between atoms in a molecule (42). The mechanical analogue then possesses the same spatial form and symmetry as the molecule, and the vibrations which it undergoes when one or more of the masses is displaced from its equilibrium position will correspond to the vibrations of the molecule.

The vibrations of a system of discreet masses are subject to analysis by the methods of mechanics. The system has 3N degrees of freedom, where N is the number of particles. Of these, three are translational, three are rotational and 3N - 6 are vibrational. When the 3N - 6 vibrational modes are expressible in terms of a set of coordinates termed the normal coordinates each vibration is independent of the others, and no interaction exists between the modes. The means by which these normal coordinates are found and the limitations of the concept of normal vibrations is the subject of a large literature (42,43). Suffice it to say here that the normal coordinate treatment of a great many of the simpler molecules has been carried out and much information regarding the form of molecular vibrations and the magnitudes of force constants between atoms has been obtained.

A series of molecules which contain in common a particular functional group or arrangement of bonded atoms frequently exhibit a common absorption in some narrow region of the spectrum. For example, molecules containing a carbonyl group show absorption in the frequency range 1850 cm.$^{-1}$ to 1650 cm.$^{-1}$, while alcohols show absorption in the range 3675 cm.$^{-1}$ to 3600 cm.$^{-1}$. It is common practice to associate such bands with a vibrational motion of the atoms in the common functional group.

The results of normal coordinate analysis show, however, that each normal vibration which gives rise to absorption involves not merely a motion of one atom with respect to a rigid structure which is the rest of the molecule, but a motion of all the atoms with respect to one another. It is true, nevertheless, that in many cases, such as the ones mentioned above, a large part of the vibrational energy resides in the atoms of the functional group associated with the vibration. This is particularly true when a light atom is vibrating against a relatively much heavier mass, as in carbon-hydrogen and oxygen-hydrogen stretching and bending modes. In the case of alcohols, which are the subject of this study, the vibration occurring at about 3625 cm.$^{-1}$ is associated with the oxygen-hydrogen stretching vibration, and may be taken to involve a motion of the hydrogen against a stationary system. For a series of alcohols, then, it may be assumed that variations in the OH band are due, not to changes in the form of the normal vibration, but to changes in the oxygen-hydrogen bond.

Not all of the normal vibrations of a molecule need be infrared active, that is, lead to absorption. In general, infrared absorption occurs when the vibration involves a change in the vector magnitude of the electric moment of the molecule. From radiation theory it may be deduced that $A_i^{i'}$, the intensity of a normal vibration which represents a transition of the molecule from the ground state i to the vibrationally excited state i' is given by

$$\text{I.} \qquad A_i^{i'} = \frac{8\pi^3 \nu_i^{i'} N}{3hc}\left[\left|U_{ix}^{i,o}\right|^2 + \left|U_{iy}^{i,o}\right|^2 + \left|U_{iz}^{i,o}\right|^2 \right]$$

where the $U_i^{i,o}$ are the matrix elements of the components of the electric moment for the transition (44).

One result of normal coordinate treatment in conjunction with considerations of statistical mechanics is that each normal coordinate may be treated as a harmonic oscillator. From this it follows that

$$\text{II.}\quad A_i^{i'} = \frac{N\pi}{3C}\left[\left(\frac{\partial\mu_x}{\partial Q_i}\right)^2 + \left(\frac{\partial\mu_y}{\partial Q_i}\right)^2 + \left(\frac{\partial\mu_z}{\partial Q_i}\right)^2\right]$$

where Q_i is the normal coordinate for the transition. When Q_i is expressed in terms of the bond coordinates, r_k, the intensity is found to be proportional to $\left(\frac{\partial\mu}{\partial r_k}\right)^2$ for a stretching vibration and to μ_k^2 for a bending vibration, where μ_k is the bond moment. Again, for a vibration such as the oxygen-hydrogen stretch, only the oxygen-hydrogen bond coordinate need be considered.

Inspection of the O-H absorption band for alcohols in solution in a solvent such as carbon tetrachloride shows that the curve representing the change in absorption with frequency is of the Lorentz type. If the absorption at a frequency is expressed in terms of the optical density, $\alpha = \mathrm{Log}\ (I_0/I)$, where I is the transmitted intensity at frequency ν, and I_0 is the transmitted intensity in the absence of solute, the absorption curve approximates the form

$$\text{III.}\quad \mathrm{Log}(I_0/I) = \frac{A^2}{(\nu - \nu_0)^2 + B^2}$$

where ν_0 is the frequency of maximum absorption, A and B are constants. An absorption curve of the form of III is shown in Figure 17. The breadth of the absorption band is the result of collisional processes occurring between the solute molecule and the walls of the cage formed by the solvent. As is evident from Figure 17, the absorption approaches zero asymptotically at wavelengths far removed from the band center.

The intensity $A_i^{i'}$ is related to the value of α at frequency ν by

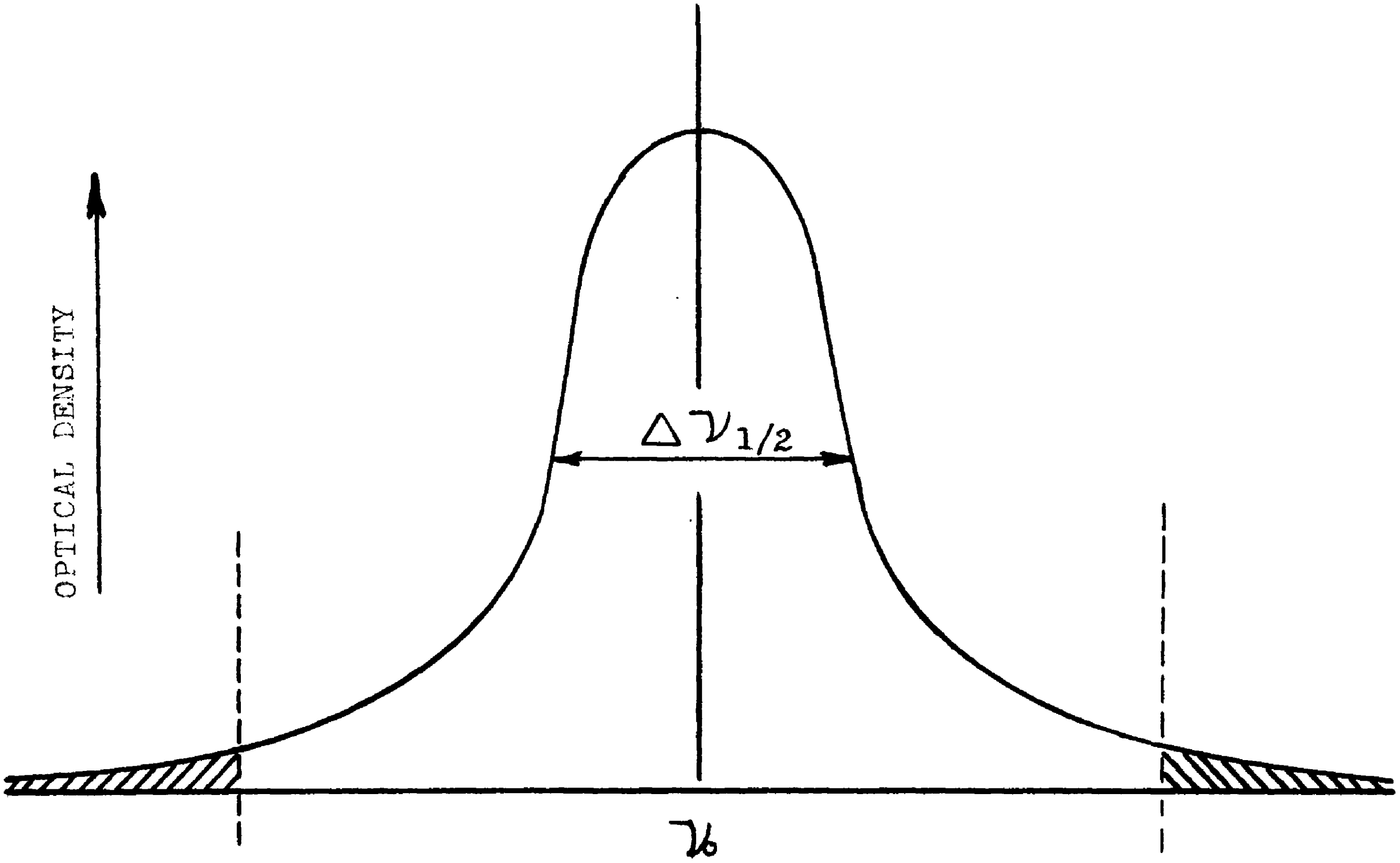

Figure 17. Characteristic absorption band for compounds in solution.

$$\text{IV.} \qquad A_i^{i'} = \frac{1}{cl}\int_{\nu_0 - \infty}^{\nu_0 + \infty} \alpha \, d\nu$$

where c is the concentration of absorbing species in moles per liter, l is the path length in cm. and ν is the frequency to which the spectrometer is set. In order to obtain the correct value for the intensity the absorption would have to be determined for frequencies far removed from band center on either side. Since the spectrometer is not capable of accurately measuring small absorptions it is not feasible to determine the absorption outside a small interval on either side of band center. This situation is illustrated in Figure 17, in which the dotted lines represent the limits of meaningful measurement. It is evident that unless a correction is made for the residual areas lying outside the interval of measurement it will not be possible to obtain the true value of the intensity.

Another problem arises in connection with Equation IV. In its most rigorous form this expression for A assumes that the spectrometer is monochromatic, whereas the instrument actually possesses a finite spectral width. The result of this is that for any particular setting of the spectrometer the observed optical density differs from the true value. The difference is dependent on the ratio of the half-intensity width, $\Delta\nu_{\frac{1}{2}}$, for the band to the spectral slit width of the instrument. The half-intensity width, shown in Figure 1, is defined as the frequency width of the band at the points where the optical density has values one-half the maximum. The spectral slit width is defined in a similar way, assuming that the plot of instrument response *vs.* frequency is an exponential curve of the Lorentz type. Ramsay has discussed the measurement of integrated intensities for compounds in solution (45). If a band shape curve of the form of III is obtained, corrections can be made for the residual absorption areas lying outside the interval of integration (wing correction). The effect of spectral slit width can also be evaluated. For the values of $\Delta\nu_{\frac{1}{2}}$ encountered in the case of the alcohols the spectral slit width employed is such that corrections for slit width are negligibly small. The wing corrections are not small, however, and for each compound studied a correction to the measured intensity must be made.

From a chemical point of view the interest in the integrated intensity of an absorption band arises from the possibility of correlating the variations in this property for a series of molecules with variations in the electronic structure.

When any or all of the nuclei are periodically displaced from their equilibrium positions the electron distribution in the molecule continuously adjusts as the internuclear distances change. This adjustment of the electron distribution is rapid in comparison with nuclear motion, so that the electron distribution may be considered to be always at equilibrium.

At present it is possible to make only qualitative statements about the changes which occur in electron distribution when any one bond in the molecule stretches. For example, in the case of alcohols, it is believed from dipole moment studies that the bond moment of the -O-H bond is the direction $O \longleftarrow\!+ H$, where hydrogen is the positive end.

The question which arises in connection with intensity measurements, however, is whether the over-all moment of the hydroxyl group increases or decreases with increasing oxygen-hydrogen distance. It is obvious from the fact that alcohols are capable of dissociation to give hydrogen ions that for large distances the moment increases with O-H distance. This is not necessarily the case for small displacements, however; arguments have been advanced for the view that the moment decreases for small increases in O-H distance (46,47). A possible solution to this problem, based more on chemical evidence than any of the previous approaches will be offered here.

The group to which the hydroxyl is attached in an alcohol will affect the intensity of the O-H band by virtue of the way in which it reacts to the change in electron distribution occasioned by the O-H stretch. This may be seen in the following way: the total wave function for the O-H group considered by itself is expressible as $\Psi = \bar{a}\,\Psi_i + \bar{b}\,\Psi_c$ where Ψ_i refers to the limiting structure A and Ψ_c to the structure B. As a first approximation it may be said

$$R - \overset{-}{O}\!:\quad \overset{+}{H} \qquad\qquad\qquad R - O : H$$

$$\text{A} \qquad\qquad\qquad\qquad\qquad \text{B}$$

that the presence of Ψ_i in the total wave function with an importance determined by the coefficient $\bar{a}$ accounts for the observed moment of the O-H bond. This is only approximately true since other contributions to the moment such as the overlap moment and the hybridization moment have been neglected (48). If, as the O-H bond distance increases, the ionic term becomes more important, the bond moment will increase with increasing O-H distance. If, on the other hand, the ionic term decreases in importance the reverse will be true. With these points in mind it is now possible to evaluate the effect of the group R attached to the hydroxyl.

The group R may affect the electron distribution in the alcohol molecule in two ways. First, the group exerts a certain polarization effect on the molecule. That is, it possesses a certain ability to withdraw or release electrons in relation to the group to which it is attached. This effect is a permanent one and affects the over-all electron distribution in the unexcited molecule, and contributes to the observed electric moment for the molecule.

In addition to this polarization, usually referred to as the inductive effect, the group also possesses polarizability properties. Under the influence of a perturbing force such as would arise from a changing internuclear distance in the molecule, the group possesses a certain ability to release or withdraw electrons as the situation demands. This polarizability is to a first approximation bi-directional; that is, the group releases or withdraws electrons with equal facility, depending on the demands made upon it. Since this is so, it is to be expected that for two groups with the same permanent polarization, or inductive, effect the intensity of the O-H band will be larger for the compound containing the more polarizable group. The reason for this is that whatever change takes place in the electron distribution in the molecule as the O-H bond stretches, leading to a change in the electric moment, the effect will be more pronounced for the more polarizable group. From this it can be said that if the polarizability properties of the group R were the controlling factor in determining the intensity variations, the intensity would be greatest for the alcohols containing the most polarizable group R. Since this does not prove to be the case, as will be seen later, it must be concluded that the permanent inductive effects and not polarizability effects are mainly responsible for intensity variations.

Using only the degree of ionic character in the O-H bond as a measure of the over-all electric moment it may be said that in order for $\frac{\partial \mu}{\partial r}$ to have a negative value the amount of ionic character in the O-H bond must decrease as the oxygen-hydrogen bond distance increases. This means that for an incremental change δr in the oxygen-hydrogen internuclear distance the center of charge for the bonding electron pair would have to move a distance greater than $\frac{\delta r}{2}$ away from the oxygen and toward the hydrogen. This movement away from the R-O group would be expected to be energetically least favorable when the group is most electronegative, that is, when the group R is most electron withdrawing. One can say then, that if $\frac{\partial \mu}{\partial r}$ is negative, the intensity, which is proportional to $\left(\frac{\partial \mu}{\partial r}\right)^2$, should be largest for the most electron releasing group. Since the experimental results show that the opposite is true, it would seem that the sign of $\frac{\partial \mu}{\partial r}$ is positive.

The validity of this interpretation depends upon the justification for neglect of other factors which contribute to the change in electric moment, namely change in overlap moment and change in hybridisation moment. The change in overlap moment is probably quite small, since the overlap moments themselves are not large. The magnitude of the change in hybridisation moment is difficult to assess. It is probably correct, however, to say that the effect of changes in the orbital hybridisation on O-H stretching will be smallest for the cases where the O-H bond is most ionic, since in these cases the bonding electron pair will most resemble energetically and spatially the unshared electron pairs occupying equivalent orbitals, and will be least affected by changes in the hydrogen distance. It is for these compounds, however, that the intensity is largest. As a result it may be concluded that the effect of orbital hybridisation changes is of minor importance in determining the intensities.

The purpose of this study of the O-H band intensity in aliphatic alcohols is to provide experimental evidence in support of the above arguments, and to provide data for the evaluation of the relative magnitudes of the effects for various groups.

HISTORICAL

There are many phases of the general problem of intensity in infrared absorption, and many of them do not relate to the type of work discussed here. Consequently only those aspects of the problem which have a bearing on the measurement of intensity for compounds in solution will be related here.

As was mentioned in the previous section, gases show a different type of absorption curve from compounds which are in a liquid medium. The gases possess rotational motion which gives rise to a splitting up of the vibrational band into a series of closely spaced narrow bands, each corresponding to a different rotational quantum number. The sum of all these lines is termed the vibration-rotation band, and the sum of the intensities of all the lines gives the absolute intensity of the vibrational transition involved. The difficulty of integrating over each of these narrow lines separately deterred earlier workers from pursuing this type of investigation. However, in 1946, E. B. Wilson and co-workers developed the theory and experimental procedure for obtaining the integrated intensity of such a band by means of pressure broadening, which involved the addition of a foreign, non-absorbing gas in sufficient pressure to cause a "smearing" of these lines together to form a single broad band (49,50). It is then necessary to scan over only the one broad band and integrate the curve obtained, applying Equation IV. This advance in technique has given rise to a considerable amount of work on vibrational bands for gaseous molecules. By means of normal coordinate analysis the values obtained for the intensities are translated into values for bond moments in the case of bending vibrations, and bond moment derivatives, $\frac{\partial \mu}{\partial r}$, in the case of stretching vibrations. It has been pointed out on several occasions in the recent literature that the results of these studies have been largely disappointing in terms of the reliability of the values obtained (51,52). As a further limitation on this type of investigation, the difficulty of carrying out an adequate normal coordinate analysis becomes great for any but the simplest molecules.

In the case of compounds in a liquid medium there is no rotational fine structure to consider, and only the single band, broadened by collisional processes appears. This band is readily integrated and, subject to the conditions outlined in the previous section, the absorption intensity is readily determined. Some of the earliest work done on liquids was done in 1935 by Wulf, Liddell and Hendricks (53).

These workers measured in a rather crude way the relative intensities of C-H and N-H overtone bands. Francis, in 1951, using a grating spectrometer with a very narrow spectral slit width measured the absorption intensities for various functional groups, including C-H and carbonyl groups (54). In 1952 Ramsay discussed the measurement of intensities for compounds in solution (45). He showed that for symmetrical bands the band shape was approximately that of a Lorentz curve, as shown in Figure 1. He discussed the problem of wing corrections and the effect of finite slit width, and the corrections which must be applied as a result of these effects.

Since it is not possible to take into account the forces which are acting on the molecule in solution a normal coordinate analysis is out of the question. The great utility of solution measurements would seem to lie in the possibility of correlating variations in intensity with structure for a series of similar molecules. Variation in intensity for a particular molecule with change in solvent properties is also a potential source of useful information.

Ramsay was able to correlate the intensities of the carbonyl band in a series of ketosteroids with various structural elements in the steroid molecule (55). Barrow showed that the intensity of the carbonyl band in a large variety of carbonyl containing compounds was related to the resonance energy in these molecules (56). More recently the same author has shown the effect of solvent change on the O-H intensity for a series of aliphatic alcohols (57). This latter paper is the only instance of work done on the O-H absorption of aliphatic alcohols.

Finally, a recent short review of intensity work lists papers dealing with other aspects of the intensity problem (58).

EXPERIMENTAL

All of the alcohols studied were obtained commercially, and were purified by drying and fractional distillation prior to use. The saturated, unsubstituted aliphatic alcohols were dried using barium oxide, and the other alcohols were dried using Drierite.

The alcohols were fractionated in a small, jacketed Vigreaux-type distillation column, a heater winding on the jacket being used to produce adiabatic conditions in the column. After discarding the first fractions of distillate a middle fraction with constant boiling point was collected and tested for purity by means of refractive index. If the refractive index was in good agreement with reliable literature values a larger sample of the fraction was collected for use. In the one or two cases where a reliable refractive index value was not available, the distillation was conducted under the optimum conditions and the large fraction having a constant boiling point and constant refractive index taken as the pure material. The alcohols were used in the intensity measurements as soon as possible after purification in order to minimize danger of contamination. The absence of water spectra in all of the samples studied confirmed the belief that the samples were dry. Table XV is a list of observed refractive indices and boiling points (uncorrected for pressure) for the purified alcohols.

Fresh bottles of reagent grade carbon tetrachloride were used in making up the samples. At the cell thickness employed in this study the carbon tetrachloride used showed no absorption in the spectral region of interest.

TABLE XV

REFRACTIVE INDICES AND BOILING POINTS FOR PURIFIED ALCOHOLS
(At atmospheric pressure unless otherwise noted.)

Compound	n_D^{20}	Boiling Point (°C.)
Methanol	1.3320	66.3
n-Propanol	1.3856	97.1
sec-Butanol	1.3968	98.7
t-Butanol	1.3870	82.5
Cyclopentanol	1.4530	139
Cyclohexanol	1.4651	160.5
Benzyl alcohol	1.5404	123 (30 mm.)
Allyl alcohol	1.4128	96
Propargyl alcohol	1.4283	112
3-Butyn-2-ol	1.4250	108.5
2-Methyl-3-butyn-2-ol	1.4212	103
3-Chloro-1-propanol	1.4474	85.5 (37 mm.)
2,2,2-Trichloroethanol	1.4850	43 (14 mm.)

The solutions employed in the measurements ranged in concentration from about 0.09 to 0.01 molar, with most of the measurements being made on solutions which were about 0.06 molar. The cell which was employed had windows of sodium chloride and was 0.494 mm. in thickness. The thickness was determined by the interference fringe method (59). A Perkin-Elmer model 21 double beam spectrometer with sodium chloride prism was employed. A mechanical slit width of 0.015 mm. was used, resulting in a spectral slit width of about 6 cm.$^{-1}$. The instrument was operated with both beam ports open, the sample cell in the sample beam, and nothing in the reference beam. Using commercially supplied recording paper inscribed with an optical density scale, the pen position was aligned to correspond to the scale on the paper. Then the instrument was operated through the spectral region of interest using only pure solvent in the sample cell. As mentioned previously, this trace showed no absorption. Then the solution was placed in the cell and the same region retraced, giving the desired absorption curve. A sample of the curves obtained in this way is shown in Figure 18.

Since the instrument employs a drive system which is linear in wavelength, it was necessary to convert the data from the chart, on which was recorded the optical density as a function of wavelength, to values of optical density <u>vs</u>. frequency in cm.$^{-1}$. This was accomplished by preparing a table in which was listed the value in frequency corresponding to each small wavelength interval on the chart. Using this table the value of optical density corresponding to each frequency was written alongside, and the table thus obtained, containing values

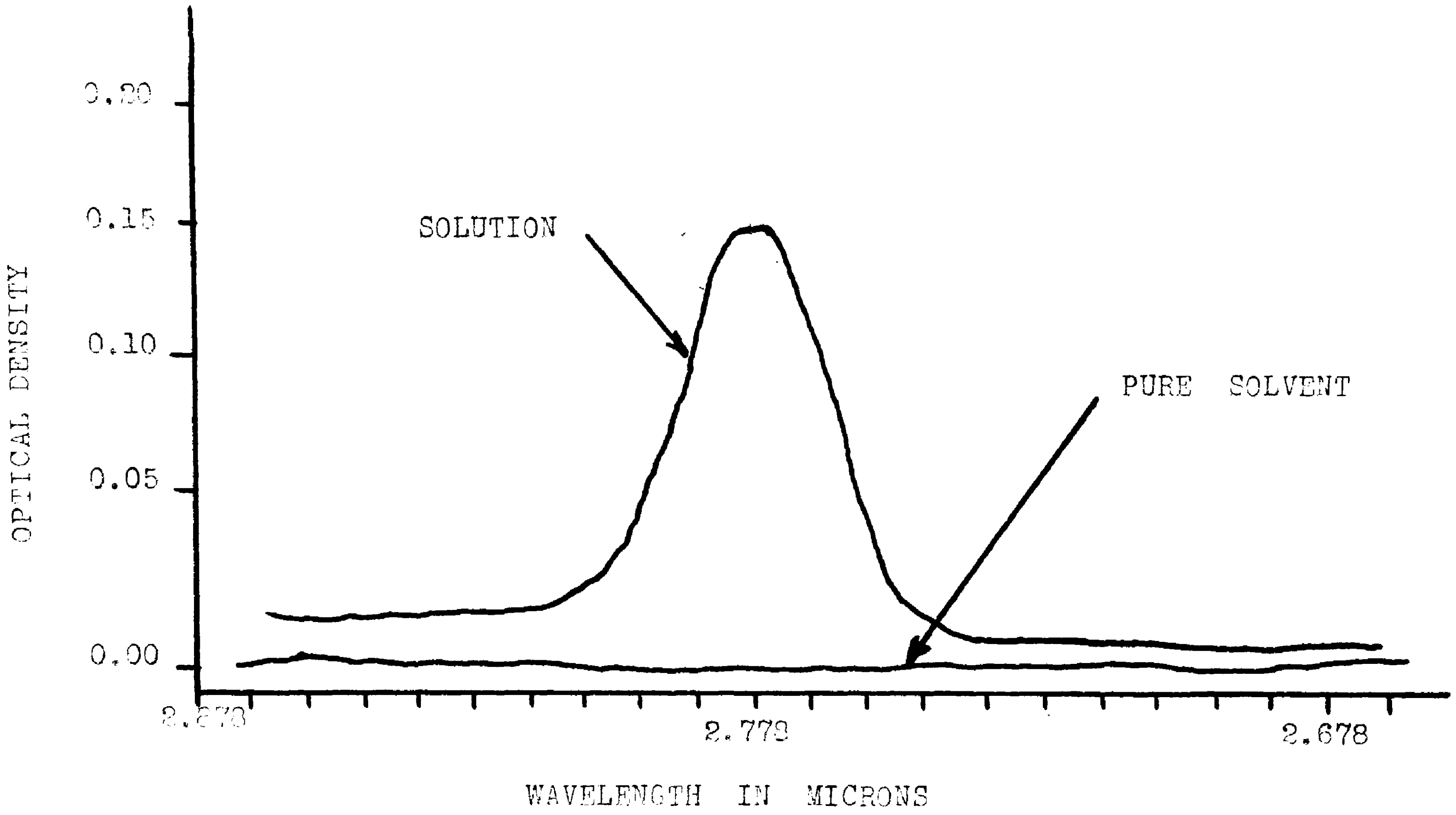

Figure 18. Curve of optical density vs. wavelength for the O-H absorption of alcohols.

of optical density *vs.* frequency in cm.$^{-1}$, was used in plotting the data on graph paper which was linear in optical density and frequency. The curve thus plotted and drawn was integrated using an Ott compensating planimeter. A rectangular area of known size was integrated for use as a standard. For curves of average area it was easy to obtain values for the area with an average deviation of 0.2%. From the value for the area in cm.$^{-1}$, determined with the use of the planimeter, the intensity was calculated by use of Equation IV. This intensity differs from the correct value, however, by the magnitude of the wing correction discussed earlier. In order to obtain the wing correction it is necessary to know the half-intensity width. This value was easily obtained from the plotted graphs. Table II of Ramsay's paper shows the percent correction for wing absorption as a function of the ratio of $\Delta\nu_{\frac{1}{2}}$ and the integration interval. This table is reproduced graphically in Figure 19 and extrapolated to larger values of percentage correction. Using the values obtained from this table the corrections to the intensity were made to give the final value, A.

No attempt was made to determine the frequencies of the band maxima accurately. The low dispersion of the sodium chloride optical system, coupled with the fact that the instrument employs a linear wavelength drive, make for a large uncertainty in the frequency in this region of the spectrum.

The validity of the corrections made may be judged in light of two criteria, the first being more rigorous than the other. First, if the curves obtained follow the Lorentz shape exactly, the corrections will

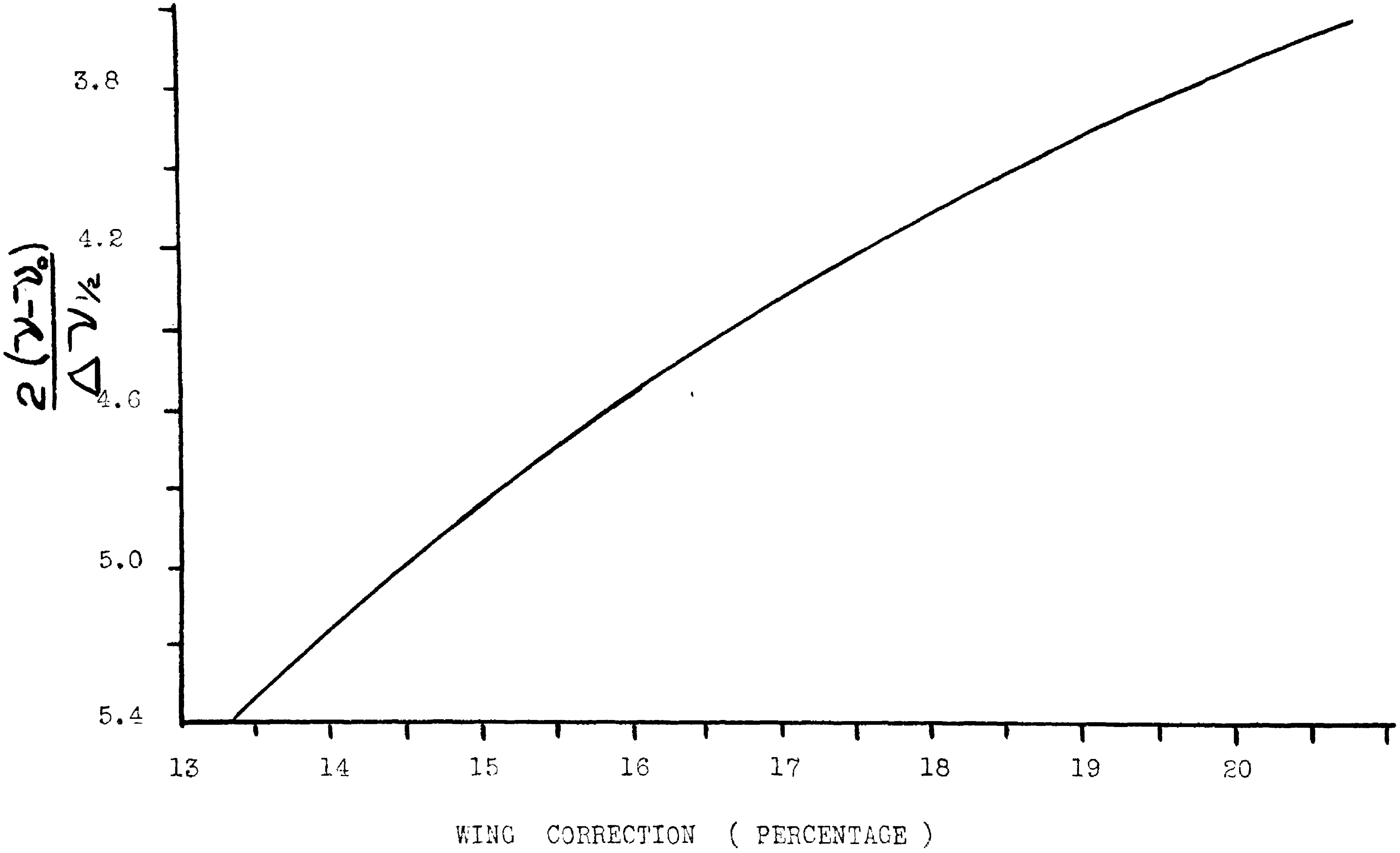

Figure 19. Ratio of integration interval to half-intensity width *vs.* percentage wing correction

be exact, and the final intensity thus obtained will equal the absolute absorption intensity to within the accuracy of the measurements. Secondly, the curves are only approximately of the correct shape, deviating in some minor respect, but the deviations for all the curves obtained being about the same. It will be seen from Figure 19 that this is the case for the curve shown; the absorption does not drop off quite as rapidly on the low frequency side as on the other side. It is to be noted that this same shape was observed for all the alcohols studied. Thus, while the corrected values for the intensity may be 1-2 percent high, it would seem reasonable to expect that the relative values for the alcohols are not appreciably affected by any small error which may be present.

Since the spectral slit width employed, 6 cm.$^{-1}$, was small in comparison with the half-intensity widths observed, about 35 cm.$^{-1}$, it is to be expected that the errors due to slit width effects will be small.

The effect of concentration needs to be discussed here because of the problem of hydrogen bonding in the alcohols. Noticeable association was observed for the more concentrated solutions examined in this study. Since the possibility existed that this association might result in a strong concentration dependence of the intensity, a sample of 2,2,2-trichloroethanol was successively diluted in the concentration range 0.0646 M to 0.0129 M and the intensity of these samples determined. It will be seen from the results of Table XVIII that there is no regular dependence of intensity on concentration. For many of the other alcohols, where a fairly large difference in the concentration of two samples occurred there was no regular concentration dependence within the accuracy of the measurements.

If a concentration dependence were to occur in this case it is to be expected that the intensities would increase as the concentration decreased. Perhaps the most important point in this connection is that all of the alcohols exhibit the same behavior, so that their relative magnitudes are essentially unaffected by any concentration dependence which does exist within the accuracy of the measurements.

The following remarks might be made regarding the over-all accuracy of the finally obtained value for the corrected intensities; the accuracy of the uncorrected value of intensity is probably 0.02 intensity units. To this is added a correction amounting in some cases to about 20%. In view of the fact that the band shape curves for all the compounds are similar, with similar values of $\Delta \nu_{\frac{1}{2}}$, giving similar correction magnitudes, it is felt that the uncertainty in the relative values of the corrected intensities is not much greater than 0.02 units.

Since the curves do not deviate from the theoretical shape by a great deal, the corrected values are probably within 5-10% of the true value for the absorption intensity.

As an example of the method outlined above, the calculations for n-propanol will be given. The data taken from the absorption curve are given in Table XVI. These are plotted on a large sheet of centimeter-scale graph paper, using 1 cm. = 5 cm.$^{-1}$ as a frequency scale and 1 cm. = 0.10 as an optical density scale. The planimeter is then used to obtain the values of the areas and the calculations outlined in Table XVII are carried out.

TABLE XVI

VALUES OF OPTICAL DENSITY *vs.* FREQUENCY AS TAKEN FROM SPECTRAL CURVE

Frequency (cm.$^{-1}$)	Optical Density (x 10^{-3})	
	I	II
3555.5	19	14
3559.5	19	14
3563.5	19	14
3567.5	19	14
3571.5	20	14
3575.5	20	15
3579.5	21	15
3583.5	24	16
3587.5	28	18
3591.5	34	21
3595.5	45	27
3599.6	60	37
3603.7	77	48
3607.8	96	60
3611.9	115	76
3616.0	135	90
3620.1	150	106
3624.2	164	120
3628.3	170	128
3632.4	164	130
3636.5	148	120
3640.6	125	98
3644.8	95	77
3649.0	69	59
3653.2	48	41
3657.4	36	26
3661.6	26	20
3665.8	22	16
3670.0	20	15
3674.2	17	14
3678.4	16	13
3682.6	16	12
3686.9	15	11
3690.2	14	10
3694.5	13	9
3698.8	12	8
3703.1	11	7
3707.4	11	7

TABLE XVII

SUMMARY OF CALCULATIONS USED IN DETERMINING THE INTENSITY OF THE O-H ABSORPTION FOR n-PROPANOL

	I	II
Concentration	0.0883 M	0.0629 M
Planimeter reading for area	1.645	1.168
Planimeter reading for standard 5.00 cm.$^{-1}$ area	0.988	0.988
Area of absorption curve	8.33 cm.$^{-1}$	5.91 cm.$^{-1}$
Uncorrected area, A', by use of the formula*	0.44_2	0.43_7
$A = \frac{2.303}{c\,l} \times \text{Area}$		
(units are mole^{-1} liter cm.$^{-2}$)		
Half-intensity width	41 cm.$^{-1}$	39 cm.$^{-1}$
Wing correction as taken from Figure 19	20.4%	19.4%
Value of corrected intensity	0.53	0.52

*The 2.303 is included to obtain the value of the intensity in terms of natural logarithms, in keeping with the usual practice.

RESULTS

Table XVIII shows the results of the intensity experiments on the alcohols. For each compound the concentrations of all samples measured are listed in the second column, the uncorrected integrated intensities in the third, the half-intensity widths in the fourth and the corrected values of integrated intensity in the fifth column. The concentration is given in moles per liter, the intensities in units of 1 x 10^{4} moles^{-1} liter cm.^{-2}, and the half-intensity widths in cm.^{-1}.

TABLE XVIII

SUMMARY OF RESULTS OF INTENSITY MEASUREMENTS ON THIRTEEN ALIPHATIC ALCOHOLS

Compound	Conc.	A'	$\Delta\nu_{\frac{1}{2}}$	A	A_{av}
Methanol	0.0590	0.43	41	0.53	0.54
	0.0708	0.45	38	0.55	
n-Propanol	0.0880	0.44	41	0.53	0.52
	0.0630	0.44	39	0.52	
sec-Butanol	0.0630	0.39	41	0.47	0.46
	0.0318	0.38	40	0.46	
t-Butanol	0.0780		31	0.40	0.39
	0.0277		26	0.38	
Cyclopentanol	0.0711	0.44	33	0.52	0.50
	0.0611	0.43	28	0.48	
	0.0760	0.44	35	0.51	
Cyclohexanol	0.0865	0.38	34	0.44	0.44
	0.0694	0.38	34	0.44	
Benzyl alcohol	0.0806	0.54	45	0.66	0.66
	0.0595	0.54	45	0.66	
Allyl alcohol	0.0496	0.48	43	0.58	0.58
	0.0284	0.49	41	0.59	
Propargyl alcohol	0.0605	0.59	36	0.70	0.69
	0.0302	0.58	35	0.68	
	0.0218	0.60	32	0.69	
3-Butyn-2-ol	0.0370	0.55	36	0.65	0.66
	0.0355	0.57	36	0.67	
2-Methyl-3-butyn-2-ol	0.0570	0.51	30	0.59	0.59
	0.0346	0.52	26	0.58	
	0.0285	0.53	31	0.60	
3-Chloro-1-propanol	0.0771	0.61	40	0.73	0.74
	0.0499	0.64	35	0.75	
2,2,2 - Trichloro-ethanol	0.0646	0.77	39	0.92	0.92
	0.0323	0.78	40	0.94	
	0.0258	0.76	41	0.92	
	0.0129	0.75	41	0.91	

DISCUSSION

Examination of the data in Table XVIII reveals that, with a few exceptions, the differences which exist in the values of integrated intensity for the various alcohols are greater than the experimental error. The ratio of the largest value of intensity to the smallest is about 2.5, indicating that the measurement is highly sensitive to structural changes in the alcohols. Electric moment values, on the other hand, do not vary over a great range for the aliphatic alcohols. It is of interest to examine the variations of intensity shown in Table XVIII in order to determine what correlations can be made with the structural characteristics of the groups attached to the O-H.

In the series of simple aliphatic alcohols (methanol through t-butanol) the intensity decreases as the electron-donating power of the alkyl groups increases, and as the polarizability increases (60). In the series propargyl, allyl, n-propyl, the intensity decreases as the electron-donating power increases and the polarizability decreases (61). These two series are typical of the many which could be established among the compounds in the table, all of which illustrate the following point: the intensity of the O-H stretching band in the aliphatic alcohols is determined almost entirely by the inductive properties of the substituent group attached to the O-H, being greatest when the substituent group is most electron-withdrawing.

By measurement of the relative intensity of alcohols the relative electron-withdrawing or donating power can be ascertained. For example, in the present work the results for 3-chloro-1-propanol and propargyl alcohol show that the electron-withdrawing power of the $CH_2Cl-CH_2-CH_2-$ group is greater than that of the $CH\ C-CH_2$ group. Similarly, the results for allyl, benzyl and propargyl alcohol show that the withdrawing power of the unsaturated hydrocarbon radicals is in the order ethynyl > phenyl > vinyl. This order is in agreement with current opinion, although the value obtained here for benzyl alcohol would put the electron-withdrawing power of the phenyl radical closer to the ethynyl than to the vinyl, whereas the vinyl and phenyl radicals are usually considered as being about the same in this respect (61).

The difference between cyclohexanol and cyclopentanol is of interest. The higher value for cyclopentanol would indicate that the cyclopentyl ring is more electron-withdrawing than the cyclohexyl, a conclusion which is in agreement with that of other workers (62).

Walsh has explained the varying inductive power in the ethyl, vinyl, ethynyl series in terms of the changing hybridization of the carbon atom (63). The bond which joins the above alkyl radicals to some other group involve the sp^3, sp^2 and sp hybrid orbitals of carbon, respectively. As the amount of s character in the orbital from carbon increases, the center of charge of the bonding electron pair moves closer to the carbon atom, resulting in an effectively more electronegative alkyl group. This same mechanism may be responsible for the change in electron-withdrawing power of the small rings, since the hybridization of the bonds to carbon is changed from the normal arrangement due to ring strain.

The question regarding the sign of $\frac{\partial \mu}{\partial r}$ for the O-H bond moment was raised in the introduction. It was pointed out there that if the sign of the derivative were positive it might be expected that the intensity would increase with increasing electron-withdrawing power of the substituent group. Since this proves to be the case it may be said that the results of these intensity studies point to a positive sign for the bond-moment derivative of the O-H bond. This conclusion is based upon the assumption that the bond moment of the O-H bond is directed toward hydrogen, with the oxygen atom as the negative end. It should be mentioned that there is some theoretical work which indicates that the opposite is true (64). The interpretation of the intensity data remains the same if this assumption is made; the sign of the bond moment derivative would then be negative, however, instead of positive.

It has been mentioned already that the only other instance of intensity measurements on aliphatic alcohols is a recent paper by Barrow (57). It is difficult to compare the results obtained here with his, but the agreement does not appear to be very good. Barrow did not state the source of his alcohols or whether the materials were purified prior to use. The interval of integration was not stated, nor was any indication given that a wing correction had been applied to obtain the listed values.

SUMMARY

PART I

A study has been made of the preparation and some physical properties of the crystalline lithium alkyls, methyl- and ethyl-lithium.

Methyl-lithium has been prepared by a new method, involving the reaction of ethyl-lithium with methyl iodide in benzene. The material obtained as a precipitate in this reaction is identical with methyl-lithium prepared by the reaction of dimethylmercury with ethyl-lithium in benzene. The infrared spectra of Nujol and perfluorokerosene mulls of solid methyl-lithium have been obtained. Microscopic and x-ray diffraction studies of the crystals reveal that methyl-lithium is of cubic symmetry, unit cell dimension $a_0 = 8.909 \pm 0.016$ Å, 16 molecules per unit cell, density 0.826 gm./cm.^{3}.

Ethyl-lithium has been prepared by causing ethyl bromide to react with lithium metal in a closed system, using pentane as a solvent. Pure crystalline material has been obtained as a product of this reaction. The infrared spectra of Nujol and perfluorokerosene mulls of solid ethyl-lithium have been obtained. Microscopic and x-ray diffraction studies of the solid material reveals that the crystals are of orthorhombic symmetry, unit cell dimensions, $a_0 = 6.65$ Å, $b_0 = 9.03$ Å, $c_0 = 8.10$ Å. There are 8 molecules per unit cell, density 0.98 gm./cm.^{3}. The space group $P222_1$ has been assigned to the crystal. Studies of benzene solutions of ethyl-lithium reveal that the material is associated about

six-fold, and that the associated configuration possess an electric moment.

PART II

The integrated intensity of the infrared absorption due to the O-H stretching vibration in a series of aliphatic alcohols has been determined. The integrated intensity in this series of compounds is strongly dependent on the nature of the alkyl group attached to the hydroxyl; it is influenced primarily by the electron-withdrawing or donating power of these groups. The intensity is greatest when the alkyl group is most electron-withdrawing. The measurement thus provides a sensitive measure of the inductive effect of the alkyl groups attached to the hydroxyl. From the manner in which the intensity varies with electron-withdrawing power of the alkyl group it can be inferred that the O-H bond becomes more ionic as the bond distance increases.

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