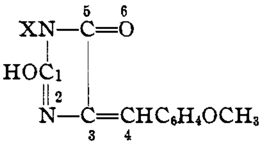
(a^1)



Molecules possessing such a configuration contain a so-called crossed conjugate system of double bonds (1-2-3-4 and 4-3-5-6) and might therefore be expected to show a selective absorption different from that of molecules containing a single conjugate system associated, as in b, with an isolated carbonyl group.

Summary

The absorption curves[14] together with other physical and chemical properties of anisalhydantoin and its N-3-substitution products as compared with N-1- or N-1-N-3- derivatives, serve to differentiate these substances into two separate and distinct groups. The suggestion is made that the differences between these groups may be due to corresponding differences in configuration.

(14) For a closer comparison of the three different types of curves see Fig. 4.

SOUTH HADLEY, MASS. RECEIVED NOVEMBER 13, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MISSOURI]

A Study of the Magneto-optic Method of Analysis

BY DONALD C. BOND

The magneto-optic method of analysis was proposed by Allison and Murphy in 1930[1] and since that time it has been used by a number of investigators, apparently with success.[2] However, there has been considerable controversy concerning the merits of the method, since many workers have been unable to duplicate the results of Allison and his co-workers. In view of the controversial status of the method, the present work was undertaken in an effort to clarify the situation.

Considerable time was spent by the author in studying the magneto-optic apparatus in use in the laboratory of Dr. T. R. Ball at Washington University, under the direction of Mr. R. E. Wingard. This equipment, which had been copied from that of Allison, was duplicated in as great detail as possible. Since it has been described elsewhere,[2] the apparatus will not be discussed further here.

After certain adjustments had been made, it was found that the Allison effect could be observed. Readings were made in the following manner. Two workers alternately observed and recorded scale readings. Every precaution was taken to prevent psychological factors from causing one scale reading to occur more frequently than another. Although it was found that the observer could seldom return to the initial scale reading or move any desired distance on the scale, even when consciously attempting to do so, nevertheless, the recorder, before each observation, moved the trolley back and forth in order to confuse the observer, finally leaving it at some random setting.

In some cases the observer desired to comment on a given reading. Thus, he might have said that it was questionable, in which case it was given a weight of one-half that of an ordinary reading. Likewise, he might have been so confident about a reading that he would want to give it a weight of two. In any case, such comments were always made *before* the scale light had been turned on and the trolley position read.

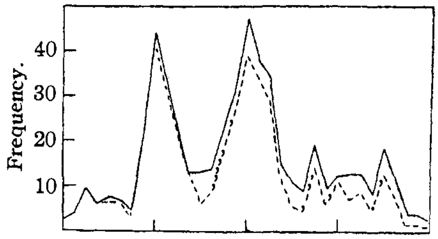
According to Allison, the "minima" for cupric chloride are found at 20.48, 20.56 and 20.68 on the scale. In Graph I (heavy line) are shown readings which were taken in the course of some work with cupric chloride solutions. All of the readings taken over a period of two months with solutions of concentration 3×10^{-12} g. of copper per cc., or greater, have been included, without any omissions. Readings taken at smaller concentrations have not been plotted because it is believed that the "minima" for cupric chloride are not present at these concentrations.

Included in this graph are several sets of readings which are known to be unreliable because it was noticed before they were taken that the line voltage was fluctuating or that the observer's eyes were tired. Although it seems that there is sufficient reason for discarding these sets, this has not been done because it might be objected that one had retained only the data which indicated the existence of an effect. Since there is

(1) Allison and Murphy, THIS JOURNAL, **52**, 3796 (1930).

(2) A complete review of the work which has been done with the magneto-optic apparatus is given by Cooper and Ball, *J. Chem. Ed.*, **13**, 210 (1936).

reasonable doubt about these readings, however, they have been omitted in the dotted line in Graph I for the sake of comparison.



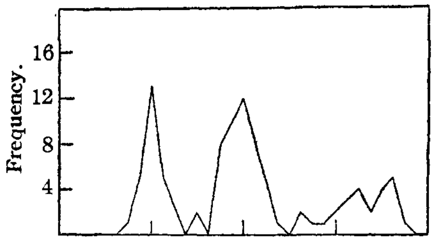
Graph I.—$CuCl_2$ "minima."

In Graph II are shown readings which were obtained with solutions of cupric chloride containing 10^{-9} g. of copper per cc. Here again all of the readings obtained with a given solution have been plotted. This graph illustrates the type of results possible with solutions whose concentrations are not near the "threshold" concentration, (these readings are included in Graph I).

The scale readings of the "minima" were found to change when the distance between the cells was changed, as reported by Allison, so that the effects observed could hardly have been caused by imperfections in the trolley system or other mechanical defects.

The magneto-optic method of analysis was applied with some degree of success to the determination of the amount of copper in a sample of phosphorescent zinc sulfide which had been prepared in these laboratories. The procedure which was used was that employed at Washington University. That is, for each solution investigated each observer moved the trolley back and forth across the position of the cupric chloride "minima" and decided whether or not the "minima" were to be seen and then the two observers compared notes. In addition, for the smaller concentrations, even in those cases in which it was thought that no "minima" could be seen definitely the scale readings of any fleeting effects observed were taken and frequency curves were plotted in the hope that these would reveal "minima" which were difficult to detect.

A number of tests were made with pure water and unknowns were run and at the time the work was done we were convinced that we could tell whether or not the "minima" were present with a given solution. In retrospect, however, it appears that there may be some doubt as to whether or not all of the insidious psychological effects possible were eliminated. While our results indicate that each Allison "minimum" is due to the presence of a certain compound, disappearing when the concentration is reduced to a very small value, we are not yet ready to say that this has been shown conclusively.



Graph II.—$CuCl_2$ "minima," 10^{-9} g. Cu per cc.

A word of apology would perhaps not be out of place here. Every paper which has appeared up to now in which the magneto-optic method has been criticized has concerned itself chiefly with the question of the reality of the "minima" observed with the apparatus. For that reason we have concentrated our efforts upon the question of the existence of the "minima," neglecting for the time a thorough investigation of the more difficult question of whether or not the "minima" disappear when the solution is diluted.

It would be difficult to say how well our observations and results compare in reliability with those of others who have worked with the Allison apparatus. Some idea of this may be obtained, however, by comparing Graphs I and II with similar graphs obtained by Ball and Crane.[3]

Miscellaneous Experiments.—A number of experiments were performed in an effort to throw some light on the behavior of the Allison apparatus and the nature of the phenomenon involved in the magneto-optic method.

A cathode-ray oscillograph was used to study the spark discharge. It was found that for each cycle of the 60-cycle a. c. supply from one to ten discharges occurred, depending upon the capacitance, voltage and gap width used. This is in agreement with the results which Cooper and Ball[2] obtained by another method. Any slight irregularity in the spark discharge is easily detected in the oscillograph, so that it is possible to obtain a much steadier discharge than by the ordinary methods. For this reason it is hoped that the oscillograph will prove a valuable accessory in the adjustment of the Allison apparatus.

A number of photographs of the magnesium spark spectrum were taken, using the color filters employed in the Allison apparatus. It was found that two lines appear, of

(3) Ball and Crane, This Journal, **55**, 4860 (1933).

about equal intensity. They are: a doublet having a wave length of 4481 Å. and a triplet whose average wave length is about 3830 Å. This result contradicts that of Cooper and Ball,[2] who found that only the 4481 Å. line passed through the filters.

The "Landolt fringe"[4] was found to be present in the Allison apparatus. Probably it is to be observed in any similar apparatus, although it has not been noticed by other workers, so far as can be learned.

When a cell filled with carbon disulfide is placed in one of the solenoids in the Allison apparatus and the solenoid is disconnected, the light from the spark can be completely extinguished by rotating the analyzer to the proper position. However, if the solenoid is connected in the condenser circuit so that the pulse from the spark passes through it, there is no setting of the analyzer for which the light is completely extinguished. That is, for the position of the analyzer which gives the most complete extinction possible, there is still a definite and unmistakable amount of light to be seen. Although this effect is no doubt to be observed in any Allison apparatus, so far as can be learned it has never been mentioned and there has been no speculation as to its cause.

This effect may be explained as follows. The passage of the electric pulse through the solenoid around the carbon disulfide cell causes a Faraday rotation of the plane of polarization of the light passing through the cell. However, the amount and direction of this rotation vary with the time, so that there is no setting of the analyzer for which the light is completely extinguished at every instant. Since the eye integrates the illumination received by it, the net effect is that light is observed at all possible settings of the analyzer.

When a carbon disulfide cell is placed in each solenoid in the apparatus, the following may be observed. If the polarities of the solenoids are in the same direction, the effect described above is greatly increased, while if the polarities are opposed, it is possible to extinguish the light completely by rotating the analyzer to the proper angle. This is, of course, what is to be expected if the above explanation holds.

It will be shown later that there is reason for believing that the light which passes through a single carbon disulfide cell in the Allison apparatus is elliptically polarized. Tests for the presence of elliptically-polarized light were made with a quarter-wave plate, a Brace half-shade,[5] and a Bravais ellipticity half-shade,[6] but none gave any definite results. Since the double refraction expected would be at a maximum in certain quadrants of the cell, the ellipticity tests were repeated on light which passed through these quadrants, without any definite, positive results. It is not surprising that these tests failed, since the double refraction anticipated probably would be as difficult to detect as the Allison phenomenon itself.

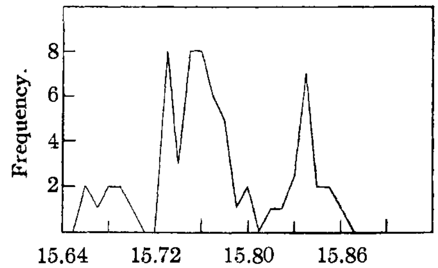
Attempts to detect a heating effect in the carbon disulfide cell in the apparatus were unsuccessful. It was estimated that any rise in temperature due to the pulsating field present in the carbon disulfide is less than 0.001° per minute.

(4) R. W. Wood, "Physical Optics," 2d ed., The Macmillan Company, New York, 1911, p. 301.

(5) Brace, *Phys. Rev.*, **18**, 70 (1904).

(6) Tronstad, *J. Sci. Instruments*, **11**, 144 (1934).

Observations were made with the polarity of one of the solenoids in the apparatus reversed and also with the analyzer rotated so that the Nicols were uncrossed. Definite evidence was found for the presence of effects which were located at the same trolley positions as those at which "minima" were ordinarily observed (Graph III). Although Allison, Christensen and Waldo[7] report that either maxima or minima of light intensity may be observed, according to the direction of the magnetic field and the position of the analyzer, we were unable to detect any difference between the appearances of the two phenomena. Considering the intangible character of the effect observed and the very great difficulty of even detecting it, one wonders whether it is possible for anyone to determine definitely whether it is an increase or a decrease in intensity.



Graph III.—HCl "minima," Nicols crossed, fields assisting.

Theoretical Discussion of the Allison Effect

Although the Allison effect was discovered almost ten years ago, the only explanation for it which has been advanced is the original hypothesis of Allison that it is caused by a differential time lag in the Faraday effect. Allison and his co-workers have performed a large number of experiments designed to test the theory of a Faraday time lag and their results support this hypothesis to a certain extent. However, there are several reasons why it is believed this theory is untenable.

In the first place, there is the fact that the results of Abraham and Lemoine[8] contradict this explanation. These results, obtained in a perfectly straightforward method, showed that any time lag in the Faraday effect for carbon disulfide must be less than 10^{-8} second. Allison has found time lags which are less than that of carbon disulfide by more than 10^{-8} seconds, indicating that the lag for carbon disulfide is greater than this.

In the second place, if the effect were due to a time lag in the Faraday rotation, it seems that it would be impossible to observe "minima" with the Nicols uncrossed, as they are actually ob-

(7) Allison, Christensen and Waldo, *Phys. Rev.*, **40**, 1052 (1932).

(8) Abraham and Lemoine, *Compt. rend.*, **130**, 499 (1900).

served, for the following reason: the rotation which takes place, if any, when the position of a "minimum" is passed must be very small indeed, since the effect is so difficult to observe. Mr. Wingard[9] suspects that a rotation of the plane of polarization of about ten minutes may be detected when an Allison "minimum" is passed, although this has not been established definitely. Now if the analyzer were set ten minutes off the position of extinction, a rotation of ten minutes toward the position of extinction might possibly be detected, since one would be observing the difference between an intensity of $I_0 \cos^2 (90° - 10')$, or $I_0 \sin^2 10'$, and an intensity of zero. (I_0 equals the intensity of light with Nicols parallel.) However, in the case in which the Nicols were parallel, as one moved past the position of a "minimum," he would have to detect a difference between I_0 and $I_0 \cos^2 10'$; that is, a difference of $I_0 (1 - \cos^2 10')$. But $(1 - \cos^2 10')$ is equal to 4.1×10^{-6}, so that a change in relative intensity of about 4.1×10^{-4} per cent. would be expected and this could hardly be detected. The fact is, of course, that an effect is observed under these conditions.

On the other hand, it can be shown in a similar manner that if the Allison phenomenon were caused by a rotation large enough to produce a perceptible effect with the Nicols uncrossed, then the effect obtained with the Nicols crossed should be extremely easy to detect, whereas the fact is that it is very difficult to detect.

There is still another objection to the theory that the Allison effect is caused by a Faraday time lag. If the phenomenon were caused by such a lag in rotation, then for a certain angular setting of the analyzer, near the angle of extinction, it would be expected that no effect would be observed, while at angles to one side of this position "minima" should be observed and at angles on the other side of this position "maxima" should be seen. However, experimentally it has been found possible to observe effects, indistinguishable from one another, with the analyzer set at the angle of most complete extinction or at any position on either side of this angle, within certain limits.

It is possible that a rotation of the plane of polarization takes place in the Allison apparatus when the trolley is moved past the position of a "minimum." It is even possible that this rotation, if it does occur, which is doubtful, is caused by a lag in the Faraday effect, but it seems that such a rotation cannot explain the Allison phenomenon.

A possible explanation of the Allison effect will now be submitted which is based upon the following assumptions:

1. The rapidly changing magnetic field present in the solenoids in the Allison apparatus is accompanied by an electric field. The presence of this electric field in the liquid inside the solenoid causes the beam of plane-polarized light to become elliptically polarized, because of the Kerr electric double refraction effect.

2. Under the influence of the magnetic field the molecules of the liquid are, to a certain degree, distorted and oriented. Likewise, under the influence of the electric field the molecules undergo a distortion and an orientation which are, in general, not the same, in magnitude and direction, as the distortion and orientation caused by the magnetic field. It may be supposed that the time which is measured with the Allison apparatus is the time required for the molecules of the liquid to change from the configuration which they have when the magnetic field is at maximum to the configuration which they have when the electric field is at a maximum.

According to the theory of electro-magnetism, a changing magnetic field is always accompanied by an electric field. This fact is expressed mathematically by the vector equation[10]

$$\nabla \times \bar{E} = -\frac{\mu}{c}\dot{\bar{H}} \tag{1}$$

where $\bar{E}$ is the electric vector, μ is the magnetic permeability, c the velocity of light and $\dot{\bar{H}}$ the time rate of change of the magnetic vector. In cylindrical coördinates $\nabla \times \bar{E}$ may be written[11]

$$\begin{aligned}\nabla \times \bar{E} &= \frac{\bar{\rho}}{\rho}\left[\frac{\partial E_z}{\partial \theta} - \frac{\partial(\rho E_\theta)}{\partial z}\right] \\ &+ \bar{\theta}\left[\frac{\partial E_\rho}{\partial z} - \frac{\partial E_z}{\partial \rho}\right] \\ &+ \frac{1}{\rho}\bar{z}\left[\frac{\partial(PE_\theta)}{\partial \rho} - \frac{\partial E_\rho}{\partial \theta}\right]\end{aligned} \tag{2}$$

where $\bar{\rho}$, $\bar{\theta}$ and $\bar{z}$ are unit vectors along the ρ, θ and z axes, respectively, and E_ρ, E_θ and E_z are the components of the electric intensity, $\bar{E}$, along the ρ, θ and z axes, respectively.

In the Allison apparatus let the z-vector be

(9) Private communication.

(10) Leigh Page, "Introduction to Theoretical Physics," D. Van Nostrand Co., New York, 1928, p. 433.

(11) Max Mason and Warren Weaver, "Electromagnetic Field," University of Chicago Press, Chicago, 1929, pp. 118 and 366.

along the axis of the solenoid and let the ρ and θ vectors lie in a plane perpendicular to the axis. From reasons of symmetry, the electric field cannot be a function of θ or of z, so

$$\frac{\partial E_z}{\partial \theta} = \frac{\partial(\rho E_\theta)}{\partial z} = \frac{\partial E_\rho}{\partial z} = \frac{\partial E_\rho}{\partial \theta} = 0 \qquad (3)$$

Equation (2) then reduces to

$$\nabla \times \bar{E} = -\bar{\theta}\frac{\partial E_z}{\partial \rho} + \bar{z}\left[\frac{\partial(\rho E_\theta)}{\partial \rho}\right] \qquad (4)$$

Combining with (1), we obtain

$$\nabla \times \bar{E} = -\bar{\theta}\frac{\partial E_z}{\partial \rho} + \frac{\bar{z}}{\rho}\left[\frac{\partial(\rho E_\theta)}{\partial \rho}\right] = -\frac{\mu}{c}\dot{\bar{H}} \qquad (5)$$

Now $\bar{H}$ is along the z-axis and has no component along the θ-direction, so, therefore, $\frac{\partial E_z}{\partial \rho}$ equals zero and we have the result

$$\frac{1}{\rho}\frac{\partial(\rho E_\theta)}{\partial \rho} = -\frac{\mu}{c}\left|\dot{\bar{H}}\right| \qquad (6)$$

This equation shows that there is a component of the electric vector along the θ-direction, that is, perpendicular to the radius line at any point, and that the magnitude of this component depends upon ρ and the rate of change of the magnetic field. In addition, of course, it may be a function of the time. Furthermore, it is obvious from reasons of symmetry that there can be no component of the electric vector along the ρ or the z direction.

It is reasonable to assume that this tangential electric field causes a Kerr electric double refraction to take place. That is, the liquid in the solenoid acts like a peculiar kind of doubly-refracting crystal in which the optic axis is at all points perpendicular to the radius line. This is illustrated in Fig. 1, where the circle represents the cross section of the cell and the arrows represent the optic axis at various points. Regardless of the question of whether there is an Allison effect, or, if so, what its cause may be, it seems that the double refraction described above should occur in the Allison apparatus.

According to assumption number two made above, the Allison effect is a measure of the time required for the molecules of the liquid to change from the configuration which they have in a magnetic field to that which they have in an electric field. Let this time be t_{CS_2} and t_{HCl} for carbon disulfide and hydrogen chloride, respectively. Further, let the time required for the light to pass from the carbon disulfide to the hydrogen chloride cell be t_0. Then suppose that at zero time one half of one of the divided pulses reaches the solenoid around the carbon disulfide, so that at a time, t_{CS_2}, a Kerr double refraction takes place in the carbon disulfide. This would cause a certain amount of light to pass the crossed Nicols. Suppose that the wire path lengths are such that the other half of the same pulse reaches the hydrogen chloride cell at a time, $t_0 + (t_{HCl} - t_{CS_2})$. Then the Kerr double refraction in the hydrogen chloride would act on the same light which was elliptically polarized in the carbon disulfide by the other half of the pulse.

If the magnetic fields were assisting and the Nicols crossed, this would cause an increase in the light intensity, since the double refraction would be increased, so that maxima should be observed at this scale reading. If the magnetic fields were opposing, the effect would be the same, for the direction of the optic axis in the doubly-refracting liquid would be unchanged. Further, these same results should be obtained whether the analyzing Nicols were set at extinction or on either side of the angle of extinction.

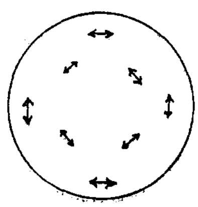


Fig. 1.

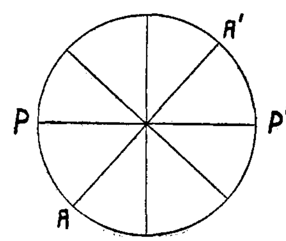


Fig. 2.

If the Nicols were parallel, or approximately so, an increase in double refraction would decrease the intensity of the light passing the analyzer. It is easily seen that in this case minima of light intensity should be observed with the magnetic fields either opposed or in the same direction, for in either case the double refraction of the hydrogen chloride would reinforce that of the carbon disulfide.

Now the effect of the double refraction would be zero in those parts of the field of vision for which the axis of the polarizer was either parallel or perpendicular to the optic axis in the carbon disulfide cell. Likewise, no elliptically polarized light would be produced in those parts of the field for which the axis of the analyzer was either parallel or perpendicular to the optic axis in the carbon disulfide. Thus, if the axis of the analyzer made an angle of 45° with that of the polarizer, the conditions would be represented by Fig. 2, where the circle is the field of view, and PP′ and AA′ are the optical axes of the polarizer and analyzer, respectively. The areas between the lines represent areas in which elliptically polarized light would be expected. It is obvious that under such conditions the double refraction would have its smallest value and it might be so small that it could not be observed. This is in agreement with the fact,[12] which is inexplicable according to the hypothesis of a Faraday lag, that the "minima" have been observed to disappear when the analyzing Nicol is rotated from the position for which it is parallel to the polarizer.

Allison, Christensen and Waldo[7] have described some experiments with the magneto-optic apparatus in which solutions possessing zero magnetic rotation were used. According to their interpretation the results indicated the presence of a Faraday time lag, but it is obvious that they may also be explained by assuming that double refraction takes place in the Allison apparatus.

Acknowledgment.—This work was suggested by Dr. Herman Schlundt and was carried out under his direction. His intense interest in the problem and his many years of careful investigation have been a continual source of inspiration.

The members of the Physics Department of the University of Missouri, particularly Dr. H. M. Reese, have constantly contributed advice, encouragement and criticism. The extent of their aid has been so great that it may be said that this is a joint production of the Physics Department and the Chemistry Department, although the Physics Department reserves judgment as to the reality of the Allison effect.

Sincere thanks are due to Mr. Perry L. Bidstrup for making many of the observations and aiding in the performance of some of the experiments.

The author also wishes to thank Dr. T. R. Ball and R. E. Wingard of the Chemistry Department of Washington University for extending the use of their laboratory and for giving so freely of their valuable information and advice.

(12) Bishop and Dollins, THIS JOURNAL, **54**, 4585 (1932).

Summary

Definite evidence has been presented for the existence of an objective effect in the Allison apparatus. Results have been obtained which indicate that this effect is caused by the presence of a particular compound, vanishing when the concentration of the compound is reduced to a very small value. However, the latter has not been proved conclusively.

Certain experiments have been described which give some information about the properties of the magneto-optic apparatus.

A partial theoretical explanation for the Allison effect has been presented.

COLUMBIA, MO. RECEIVED NOVEMBER 5, 1936

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF MELBOURNE]

Atomic Radii from Parachor Data and from Electron Diffraction Data

BY N. S. BAYLISS

Introduction

Although the parachor[1] is the most nearly additive of all "additive" properties of liquids, it has always suffered from the lack of a clear physical interpretation. Sugden, the discoverer of the function, considers it to be a measure of molecular volume, but this interpretation has been disputed by others.[2] Attempts at a theoretical treatment[3] of the parachor have not succeeded in supplying an interpretation, and without a considerable advance in our knowledge of the theory of the liquid state, it would seem impossible to obtain one on purely theoretical grounds.

By making use of the available data on atomic and molecular dimensions, it is now possible to show that Sugden's original interpretation may be applied with marked success. It will be shown in this paper that by assuming that atomic parachor constants are a direct measure of atomic volumes, it is possible to calculate atomic radii that are in good agreement with the values obtained by the electron diffraction and X-ray methods.

(1) (a) Sugden, "The Parachor and Valency," G. Routledge and Sons, London, 1930; (b) *J. Chem. Soc.*, **125**, 1185 (1924).

(2) (a) Ferguson, *Nature*, **125**, 597 (1930); (b) Desreux, *Bull. soc. chim. Belg.*, **44**, 249 (1935).

(3) Kleeman, *Phil. Mag.*, [6] **21**, 92 (1911); Eucken, *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse*, 340 (1933).