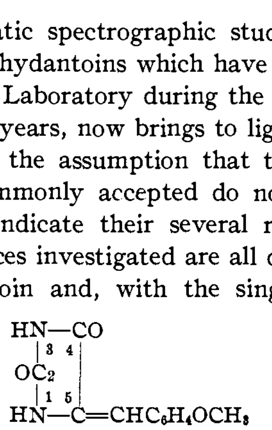
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MOUNT HOLYOKE COLLEGE]

Notable Differences in the Absorption Curves of Certain Groups of Unsaturated Hydantoins

BY MARGARET K. SEIKEL[1]

A systematic spectrographic study of certain unsaturated hydantoins which have been synthesized in this Laboratory during the course of the past twenty years, now brings to light additional evidence for the assumption that the structural formulas commonly accepted do not serve adequately to indicate their several relationships.[2] The substances investigated are all derivatives of anisalhydantoin and, with the single exception



of anisalhydantoin-N-1-acetic acid,[3] were obtained from anisalhydantoin by the direct replacement of the hydrogen atoms in the N-1- and N-3-positions. In each case the structural formulas of these substances were reported in the literature as identical with that represented above except for the fact that the hydrogen atoms in the N-1- or the N-3-position or in both were shown to have been replaced.

It now seems desirable, however, to review the data from a somewhat different angle, since a more extended study of the ultraviolet absorption spectra of a number of related compounds has made it possible to correlate consistent differences in both physical and chemical properties in such a way as to classify these compounds in separate groups. This is illustrated in Figs. 1, 2 and 3.[4] A comparison of the curves represented in Fig. 1 shows for example that the characteristic spectrum of anisalhydantoin remains almost unchanged as the result of substituting a variety of different residues for the hydrogen atom in the N-3-position. This uniformity corresponds to other similarities observed in both physical and chemical properties since all the substances whose absorption curves have been plotted, as well as other N-3-derivatives, possess many characteristics in common. For example, they all agree in being only slightly soluble in most boiling organic solvents, such as CH_3OH, C_2H_5OH, CH_3COCH_3, $CHCl_3$ and dioxane and only moderately soluble in boiling acetic acid. All represent remarkably stable compounds and have resisted every attempt to isomerize them.

On the other hand, the replacement of hydrogen in the N-1-position is accompanied by a distinct change in the absorption curve. This holds true whether the hydrogen atom in the N-3-position has been replaced or not. Here again the substitution of different groups appears to have very little effect upon the character of the absorption, as is evident from a comparison of the curves in Figs. 2 and 3. The latter represent respectively groupings of stable and labile geometrical isomers.[5] Here again the remarkable uniformity in the absorption of quite different compounds corresponds to similarities in other physical and chemical properties. For example, all dissolve readily in cold chloroform and are in general much more soluble than the corresponding N-3-derivatives so that they easily can be separated from them.[6] They are also much less stable.[7] Moreover they isomerize readily.[8]

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[1] In collaboration with Dr. Dorothy A. Hahn and Dr. Emma P. Carr.

[2] This assumption has long been the subject of informal discussion because of noticeable differences observed in the properties of two distinct groups of such compounds.

[3] This substance was prepared by condensing anisaldehyde with hydantoin-N-1-acetic acid, Renfrew and Johnson, THIS JOURNAL, **51**, 1787 (1929).

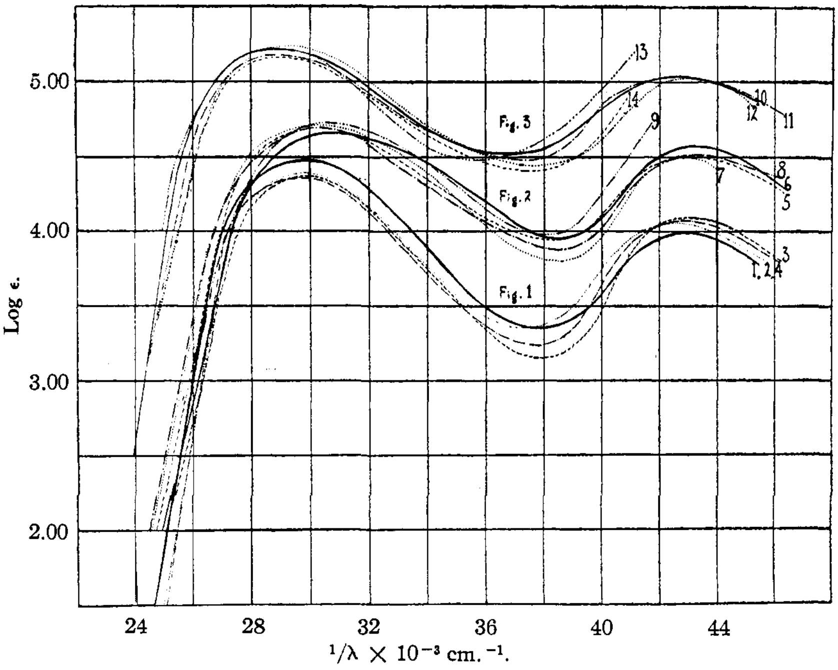
[4] Compare Figs. 1, 2 and 3 in the accompanying chart. For purposes of brevity only a few of the absorption curves which have been plotted were selected, but all which were measured fall into the same classifications.

[5] No curve for the labile isomer of 8 is given because the amount of material available at the time was not sufficient to permit the required number of recrystallizations. All substances in this group isomerize more or less in solution so that losses are sustained during the process of purification. In the case of 14 only one modification of the two possible isomers was obtained by Miss Renfrew. The fact that the absorption curve of this compound belongs obviously in this group, is of considerable importance since it, unlike all the others, contains a *free hydrogen atom* in the N-3-position.

[6] Note the relative differences in the solubilities of N-3-methyl-anisalhydantoin as compared with ethyl N-3-methylanisalhydantoin-N-1-acetate [Hahn and Renfrew, THIS JOURNAL, **47**, 151 (1925)] or with ethyl N-3-methyl-anisalhydantoin-N-1-phenylacetate [Hahn and Dyer, *ibid.*, **52**, 2498 (1930)]. It may be added that N-1-N-3-dimethyl-anisalhydantoin is also very soluble.

[7] They hydrolyze slowly on standing or rapidly in the presence of even traces of alkali. This is accompanied by the splitting off of groups in the N-1-position and to a lesser extent of groups in the C-5-position.

[8] In most cases the stable isomers are formed as a result of condensation reactions in an alkaline medium and are subsequently isomerized in alcohol solutions under the action of hydrogen chloride [Hahn and Gilman, THIS JOURNAL, **47**, 2953 (1925)]. In the case of 14 condensation in an acid medium resulted in formation of the labile modification. While the latter was the only compound which was separated from the reaction mixture, the fact is significant that only very low percentage yields were obtained since equilibrium mixtures of any two isomers frequently form oils and are then extremely difficult to separate.



All three groups of curves have been plotted on the same coördinates but in order to facilitate their comparison by representing all on one plate, the curves grouped in Figs. 2 and 3 have been raised 1 and 2 spaces, respectively. The values given for log ε therefore apply only to the curves grouped in Fig. 1.

Fig. 1.—Anisalhydantoin and its N-3-substituted derivatives: 1, anisalhydantoin, $\overline{\text{NHCOCHCOC}}{=}\text{CHC}_6\text{H}_4\text{OCH}_3$, m. p. 243–244°[a]; 2, N-3-methyl-5-anisalhydantoin, $\underline{\text{NHCON(CH}_3\text{)COC}}{=}\text{CHC}_6\text{H}_4\text{OCH}_3$, m. p. 218°[b,c]; 3, methyl 5-anisalhydantoin-N-3-acetate, $\underline{\text{NHCON(CH}_2\text{COOCH}_3\text{)COC}}{=}\text{CHC}_6\text{H}_4\text{OCH}_3$, m. p. 183–184°[d]; 4, methyl 5-anisalhydantoin-N-3-propionate, $\underline{\text{NHCON(CH(CH}_3\text{)COOCH}_3\text{)COC}}{=}\text{CHC}_6\text{H}_4\text{OCH}_3$, m. p. 163–164°[d].

Fig. 2.—N-1-N-3-Derivatives of anisalhydantoin, stable isomers: 5, dimethylanisalhydantoin. $\underline{\text{N(CH}_3\text{)CON(CH}_3\text{)COC}}{=}\text{CHC}_6\text{H}_4\text{OCH}_3$. m. p. 91–92°[b,d]; 6. ethyl N-3-methyl-5-anisalhydantoin-N-1-acetate, $\underline{\text{N(CH}_2\text{COOC}_2\text{H}_5\text{)CON(CH}_3\text{)COC}}{=}\text{CHC}_6\text{H}_4\text{OCH}_3$. m. p. 107–108°[c]; 7, methyl N-1-methyl-5-anisalhydantoin-N-1-acetate, $\underline{\text{N(CH}_3\text{)CON(CH}_2\text{COOCH}_3\text{)COC}}{=}\text{CHC}_6\text{H}_4\text{OCH}_3$. m. p. 84–85°[d]; 8, methyl N-1-methyl-5-anisalhydantoin-N-3-propionate, $\underline{\text{N(CH}_3\text{)CON(CH(CH}_3\text{)COOCH}_3\text{)COC}}{=}\text{CHC}_6\text{H}_4\text{OCH}_3$, m. p. 103–104°[d]: 9, ethyl N-3-methyl-5-anisalhydantoin-N-1-phenylacetate, $\underline{\text{N(CH(C}_6\text{H}_5\text{)COOC}_2\text{H}_5\text{)CON(CH}_3\text{)COC}}{=}\text{CHC}_6\text{H}_4\text{OCH}_3$, m. p. 119–120.5°.[e]

Fig. 3.—N-1- and N-1-N-3- derivatives of anisalhydantoin, labile isomers: 10. isomer of 5. Fig. 2, m. p. 127.5–128.5°[d]; 11. isomer of 6, Fig. 2, m. p. 127–128°[c]: 12. isomer of 7, Fig. 2. m. p. 129.5–131°[d]; 13, isomer of 9, Fig. 2. m. p. 100.5–101.5°[e]; 14, anisalhydantoin-N-1-acetic acid, $\underline{\text{N(CH}_2\text{COOH)CONHCOC}}{=}\text{CHC}_6\text{H}_4\text{OCH}_3$, m. p. 215° (223°[f]).

(a) Wheeler and Hoffman. *Am. Chem. J.*, **45**, 375 (1911). (b) Johnson and Nicolet, *ibid.*, **47**, 469 (1912). (c) Hahn and Renfrew, THIS JOURNAL, **47**, 149 (1925). (d) Hahn and Gilman, *ibid.*, **47**. 2959–60 (1925). (e) Hahn and Dyer, *ibid.*, **52**, 2497 (1930). (f) Renfrew and Johnson, *ibid.*, **51**, 1787 (1929).

In comparing the absorption curves of these three groups of hydantoin derivatives, the most pronounced difference is in the greater persistence of the long wave band in the case of the unsubstituted and N-3 substituted compounds (Fig. 1). This fact together with the higher intensity of the maximum of this band serves to differentiate compounds of this type from the N-1 or N-1-N-3 derivatives where the corresponding band is more shallow and the extinction coefficient of the maximum is distinctly lower. In the case of the stable isomers of the latter type (Fig. 2) the absorption curves start at very nearly the same frequency as that observed for the N-3-substituted derivatives but, in general, the maximum of the first band is shifted slightly toward the ultraviolet in the N-1 and N-1-N-3 compounds. The position of the second maximum remains practically unchanged for all three groups of compounds. The absorption curves of the labile isomers (Fig. 3) are very

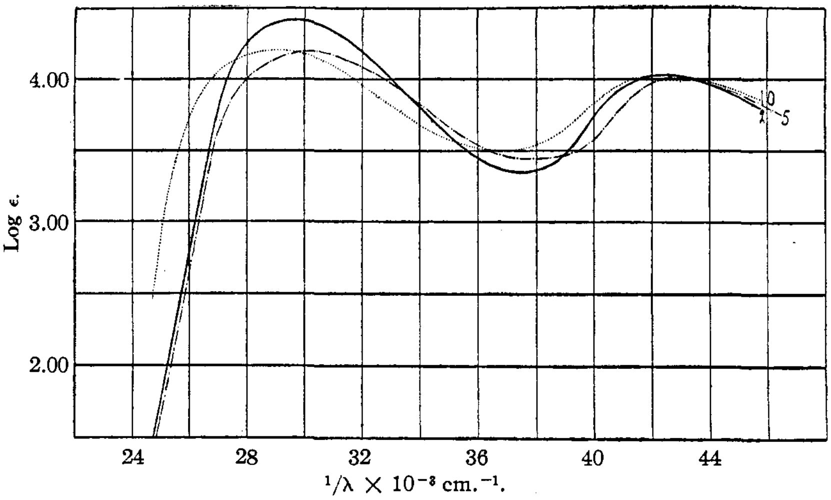
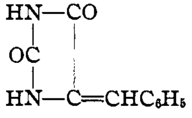


Fig. 4.—A closer comparison of: 2, N-3-methyl-5-anisalhydantoin, Fig. 1; 5, N-1-N-3-dimethyl-5-anisalhydantoin, Fig. 2; and 10, isomer of 5, Fig. 3.

similar to those of the corresponding stable modifications throughout their entire course but are shifted slightly toward the visible. These differences are so well defined that it is possible to identify a given isomer as a stable or a labile modification by means of its absorption curve. The same general relationships hold for the corresponding derivatives of benzalhydantoin

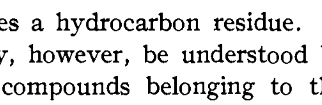


although the absorption curves of all of these compounds are shifted slightly in the direction of the ultraviolet.[9]

With the single exception of anisalhydantoin-N-1-acetic acid,[10] the compounds referred to in this paper were prepared in this Laboratory[11] and all were carefully recrystallized before using. The determinations of the absorption coefficients were carried out in alcohol solution by the Henri method using a Hilger quartz spectrograph (E 2), the procedure being essentially the same as that described by Hahn and Dyer.[12]

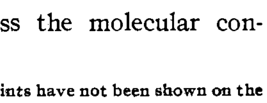
Since differences in absorption are commonly conceded to correspond to differences in molecular configuration and since the absorption of anisalhydantoin and its N-3-substitution products as a group is distinctly different from the absorption of the N-1- and N-1-N-3 derivatives, it seems probable that the two groups possess certain structural differences which are not fully indicated by the commonly accepted general formulas

(a)



and

(b)



where X denotes *either* H[13] or R, and where R denotes a hydrocarbon residue. These differences may, however, be understood by assuming that *all* compounds belonging to the first group, *a*, exist chiefly in the form of their *enolic* modifications and therefore possess the molecular configuration

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(9) Unpublished work except for Hahn and Evans, THIS JOURNAL, 50, 809–10 (1928).

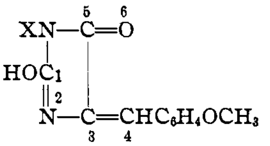
(10) Furnished through the courtesy of Renfrew and Johnson.[3] In this connection it may be noted the absorption curves of free acids are practically identical with those of the corresponding methyl and ethyl esters. For examples see Hahn and Dyer, *ibid.*, 52, 2507 (1930).

(11) References to the methods used in the preparation of all of these substances together with their respective properties will be found in the footnotes accompanying each figure.

(12) Hahn and Dyer, THIS JOURNAL, 52, 2511 (1930). It may be noted that the work of Hahn and Dyer was repeated for purposes of comparison and also in order to follow the absorption far enough into the ultraviolet to show the existence of the second absorption band. Eastman No. 40 and Ultraviolet Sensitive Plates were used, and a copper–silver spark. Each curve is based on at least 100 experimental points but these individual points have not been shown on the curves since they are so closely spaced as to give practically a continuous line. A relatively large number of compounds were investigated but the absorption curves of only 14 are represented. These are differentiated by numerals on the charts and in the text.

(13) Although anisalhydantoin-N-1-acetic acid, 14, was the only substance examined which contained a free hydrogen atom in the N-3-position, the fact appears to be highly significant that its spectrum is essentially the same as in cases where the hydrogen in this position has been replaced by a variety of different substituents. This would seem to indicate that the characteristic spectrum of all of these compounds is determined by the presence of a substituent in the N-1-position.

(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.

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[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

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[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).