When the moment of 6.10 for α-nitrotetronic acid is compared with that of tetronic acid 4.80, and that of α-chlorotetronic acid 5.83, it is apparent that there is a factor present in the nitro compound that is not present in the other two. The carbon–chlorine moment is about 1.5–1.8. The moment of α-chlorotetronic acid is 1.03 units higher than that of tetronic acid which seems reasonable in that the carbon–chlorine moment most probably is not directly in line with the resultant moment of the rest of the molecule. The large moment of the nitro group, 3–4, is directed along the carbon–nitrogen bond in the same direction in the nitro compound as the carbon–chlorine moment is directed in the corresponding chloro compound. This means that the moment of the nitro compound should be 1.5–2 units greater than that of the chloro compound. Actually it is only 0.27 unit greater which suggests some factor being present in the nitro compound which changes the direction and(or) magnitude of the moment of the nitro group. The formation of a hydrogen bond to one of the oxygens of the nitro group would have such an effect. Thus the dipole moment as well as the dissociation constant is consistent with the presence of a hydrogen bond in the enol form.

Experimental

The pH values of the solutions were measured with a glass electrode in connection with the pH meter of Goyan, Barnes and Hind.[6]

The dielectric constant measurements were carried out as described previously,[7] as was the purification of the dioxane.

The α-nitrotetronic acid had an equivalent weight of 145.5 and a melting point of 183–184° with decomposition.

The moment also was calculated by a method described previously[8] using the equations

$$p_{2_0} = \frac{3\alpha v_1}{(\epsilon_1 + 2)^2} + (v_1 + \beta) \frac{(\epsilon_1 - 1)}{(\epsilon_1 + 2)}$$
$$P_{2_0} = p_{2_0} M_2$$
$$\mu = 0.0127 \sqrt{(P_{2_0} - P_{E2_0})T}$$

The dielectric constants were linear with the weight fractions indicating no association effects in the solutions.

Summary

α-Nitrotetronic acid has a pKa of 1.68 and a dipole moment of 6.10. From considerations of general stability the enol form is more probable than the isonitro structure. Both the dissociation constant and the dipole moment are consistent with the presence of a strong hydrogen bond in the enol form.

(6) Goyan, Barnes and Hind, *Ind. Eng. Chem., Anal. Ed.,* **12**, 485 (1940).

(7) Kumler and Halverstadt, THIS JOURNAL, **63**, 2182 (1941).

(8) Halverstadt and Kumler, "A Critical Study of Dielectric Polarization Curves," in publication.

The Absorption Spectra and the X-Ray Examination of the Isomeric Glucononitriles

BY PHILIPPOS E. PAPADAKIS

Two forms of glucononitriles are known[1a,2,3] melting at 120.5 and 145°, and obtained by crystallization from absolute alcohol and glacial acetic acid, respectively.[3] Aqueous solutions of the two forms have initially practically the same specific rotation, but whereas that of the high melting form, to be now referred to as the A form, remains unchanged with time, that of the low melting B form shows a complex time-dependence. The present report describes investigations on the X-ray diffraction and absorption spectra of the two modifications, in an attempt to discover the reason for this contrast in behavior. Three samples of the B form,[3] checked as to melting point and microcombustion analysis, served as material.

X-Ray Examination.—Specimens of the two forms A and B were subjected to X-ray powder analysis using focusing cameras of the Bohlin type as modified by Phragmen. Possible atmospheric action was prevented by enclosing the samples in sheaths of regenerated cellulose which themselves gave no diffraction pattern. Twenty-seven lines were observed between θ values of 15 and 45° on the photograms of both specimens, corresponding in the two cases in position and intensity. These experiments within their limits of resolution did not help much in answering the problem.

(1) Original manuscript received August 15, 1940.

(1a) Zemplén, *Ber.,* **60**, 171 (1927).

(2) Wohl and Wollenberg, *Ann.,* **500**, 281 (1932).

(3) Papadakis and Cohen, THIS JOURNAL, **60**, 765 (1938).

Ultraviolet Absorption Spectra.—The absorption spectra of aqueous solutions of the A and B forms were examined by means of a small Hilger quartz spectrograph and a continuous hydrogen source. The molar extinctions were evaluated, with a precision of some 3 or 4% in the value of ϵ, by the method of Stücklen,[4] with the use of potassium nitrate as standard. Microdensitometer tracings were made of the plates by means of the Moll microdensitometer, and wave lengths were measured on these tracings.[5]

The B form in aqueous solution showed an absorption band with a maximum at 2780 Å. and log ϵ_{max}. of 0.9, besides a region of short wave absorption extending into the Schumann region. The band at 2780 Å. was present at full intensity in spectra taken as soon as possible after addition of the solid to water and persisted on standing for ten months. The characteristic band of the B form gradually disappeared on crystallization from pure acetic acid, which favors the A form, and returned on recrystallization from alcohol. The A form had no band near 2780 Å. Its spectrum was like that of β-hydroxypropionitrile and the substance was assumed to have a straight chain structure. The absorption spectra of boiled aqueous solutions of the A form showed considerable change, with a shift of the beginning of the further ultraviolet absorption toward the longer wave lengths. No such change was observed with unboiled solutions.

Although all specimens of the B form showed a band in the neighborhood of 2780 Å., irrespective of the time elapsed since the preparation of the solution, there were, nevertheless, changes in the details of the band with time. Approximately 0.113 M solutions of the B form were examined at various thicknesses and with an exposure of ten seconds. The plot of log ϵ molar against λ (Fig. 1) shows the curves 1, 2, 3 and 4 as a function of time. Four preparations gave similar curves. The characteristic band broadened with time, especially on the short wave side, and the beginning of the further ultraviolet band shifted first to longer wave lengths and then reverted to shorter. The absorption maxima[6] of the characteristic band in curves 1, 2, 3 and 4 as measured are 2780, 2775,
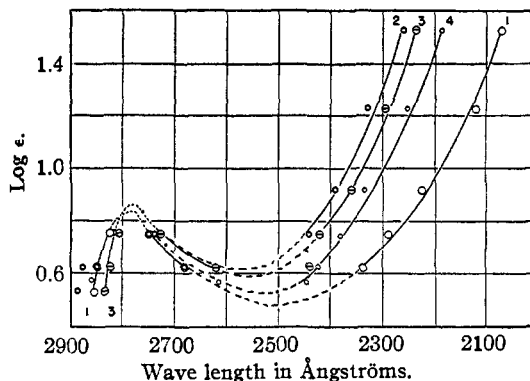

Fig. 1.—Time from mixing gluconitrile and water. Spectra photographed for Curve 1, first one-half hour; Curve 2, after twenty-five hours; Curve 3 after seventy-three hours; and Curve 4 after 672 hours.

2770, 2750 and the absorption minima 2510, 2535, 2525 and 2530, respectively.

Curves 1 and 2 of Fig. 2 are for a more dilute solution, 0.056 M in a cell 3.5 cm. long, photographed, respectively, one and 233 minutes from the time of mixing with water. These solutions showed evidence of discrete band structure, with bands at about 2730, 2678, (2608) (2530) for curve 1 and 2723, 2662, 2608 and 2530 Å. for curve 2, which became more distinct with time. Other preparations in similar conditions showed a hint of these bands, but not so distinctly as in the plate for which the curves of Fig. 2 were obtained. These bands caused the apparent maximum of the general band to shift toward the shorter wave lengths.

Scission of Hydrogen Cyanide from Gluconitrile.—In explanation of the change in rotation of aqueous solutions of gluconitrile with time, Dr. M. L. Wolfrom of the Ohio State University has suggested the possibility of the formation of d-arabinose, which has a negative rotation, by the loss of hydrogen cyanide. Pure nitrogen was bubbled for four and one-half hours through 10 cc. of an aqueous solution containing 0.4 g. of the gluconitrile and the gas evolved was passed through silver nitrate solution. A precipitate shown to be silver cyanide was collected and found to weigh 0.028715 g. The corresponding amount of d-arabinose was calculated to be 0.03216 g. This amount, dissolved in 10 ml. of water and examined in a 1-dm. tube, would have contributed rotations of -0.17, -0.57 and $-0.34°$, respectively, if present in the α,β or mutarotated form.[7]

(4) Stücklen. *J. Opt. Soc. Am.*, **29**, 37 (1939).

(5) The apparent extinction coefficients in Fig. 1 were computed on the assumption that the absorbing material was a pure substance at the stoichiometric concentration of gluconitrile.

(6) The absorption maxima and minima were determined from microphotometer tracings of respective spectra of the plates representing solutions of smaller depth. The extinction due to the band in these spectra was not complete and the microphotometric tracings afforded well-defined maxima and minima.
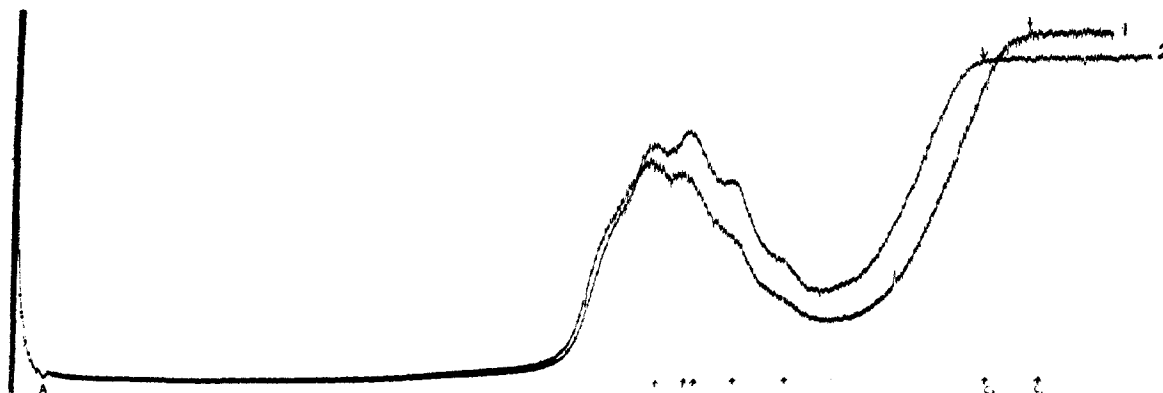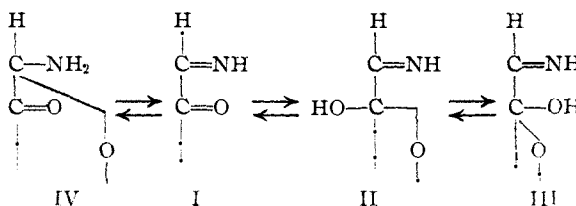
(7) The calculations were based upon the values for the specific rotations found by Hudson and Yanowski. THIS JOURNAL, **39**, 1013 (1917).

Fig. 2.—Microphotometric curves 1 and 2: A = H_h = 4861·327 Å.; C_1 and C_2 are beginnings of continuous absorption respectively.

Since the calculated drop in the rotation of the 4% solution of gluconitrile was approximately 1.40° (l = 1), the scission of hydrogen cyanide, even when favored by the passage of nitrogen, was not sufficient to account for all the change.

Discussion

The foregoing work showed that the essential difference between the absorption spectra of aqueous solutions of the A and B forms of glucononitrile is that the former has the type of spectrum to be expected of a hydroxy nitrile while the latter has a characteristic band at about 2780 Å., which may be due to some group not present in the A form. Hydrolysis products of the nitrile, as ammonium gluconate, gluconamide, glucono-γ or δ lactone or gluconic acid are not responsible for the characteristic band, since these substances,[8a] as has been verified in the course of this work, have no band near 2780 Å. Arabinose (see previous paragraph) is also without characteristic absorption in this region.[9] It seems necessary to seek for some chromophoric group which might result from internal changes in the glucononitrile molecule as the origin of the 2780 Å. band. Aliphatic aldehydes or ketones are known to have a band in this region, regarded as characteristic of aldehydic or ketonic carbonyl. The practical identity in the spectra of benzophenone and benzophenonimine[10] suggests that the C=NH group absorbs like carbonyl, and the iminolactone forms of imino-gluco-ascorbic[11] and imino-galacto-ascorbic acid have a strong band

with a maximum at 2750 Å. A 1-imino-glucosone structure previously suggested[3] (formula I), on mutarotation might give II and III, while mutarotation involving the imino group might give the ketone derivative IV. Compound I by analogy

$$
\begin{array}{cccc}
\text{H} & \text{H} & \text{H} & \text{H} \\
| & | & | & | \\
\text{C—NH}_2 & \text{C=NH} & \text{C=NH} & \text{C=NH} \\
| & | & | & | \\
\text{C=O} & \rightleftarrows \ \text{C=O} & \rightleftarrows \ \text{HO—C—} & \rightleftarrows \ \text{C—OH} \\
| & | & | & \text{\textbackslash} \\
\text{O} & \text{O} & \text{O} & \text{O} \\
\text{IV} & \text{I} & \text{II} & \text{III}
\end{array}
$$

to glucosone[8b,12] may show selective absorption at a wave length somewhat higher than 2780 Å. Compounds II, III and IV may absorb at or near 2780 Å., by analogy with the behavior of aldehydes and ketones, and their interconversion might cause both the optical rotational changes and the changes in the characteristic band. The changes with time of the long wave side of the far ultraviolet band may be due to such interconversion products. Although the formation of hydrolysis products[8,9] could not account for the absorption band at 2780 Å., the possibility of slow hydrolysis may have an effect on the changes observed in the short wave spectrum. Analysis of aged sirups of form B evaporated at room temperature and dried at 80° and *in vacuo* showed that loss of nitrogen had occurred which could not be explained by assuming a loss of hydrogen cyanide. The changes observed in the short wave spectrum curves 1, 2, 3, and 4, Fig. 1. are compatible with the relative position of the spectrophotometric curves from glucononitrile, gluconyl-d-lactone, gluconamide and ammonium gluconate. In addition, the shift of the beginning

(8) Bednarczyk and Marchlewski. *Bull. intern. acad. polon. sci., Classe sci. math. nat.* (a) 1937A. 140 in English; (b) 1938A. 524.

(9) Kweicinski and Marchlewski, *Bull. soc. chim.,* 45, 591–611 (1929).

(10) Meisenheimer and Dorner. *Ann.,* 502, 164 (1933).

(11) Haworth. Hirst. Jones and Smith. *J. Chem. Soc.,* 1192 (1934).

(12) Guillaume and Lardy. *Compt. rend.,* 176. 1548 (1923).

of the further ultraviolet absorption of boiled aqueous solutions of form A may suggest hydrolysis. On account of the inconclusive evidence concerning the question of the slow hydrolysis of the B form, it is not possible at present to associate the spectral observations with the details of the chemical changes and the problem requires further investigation.

Finally a suggestion may be made on the origin of the different melting points of the two forms. Glucononitrile may resonate between the structures $RC{:}{:}{:}N{:}$ and $RC^+{:}$ $:\ddot{N}{:}^-$ as the alkyl cyanides are supposed to do.[13] The rather ionic character of the CN group might then lead to the formation of hydrogen bonds between the highly electro-negative hydroxyl oxygen and the nitrogen atoms. According to Thompson's infrared investigations[14] intermolecular bonding is more prominent in liquid hydroxy nitriles. As the presence of intermolecular hydrogen bridges is associated with higher melting points than their absence,[13] it seems plausible to associate the high melting point of the A form with the presence of intermolecular hydrogen bonds, while in the B form the bonds are either weaker or of the intramolecular type. More direct information on this question might be gained from a study of the infrared spectra of appropriate glucononitrile derivatives in which all but one hydroxyl group is blocked.

The author wishes to express his thanks to Dr. Wm. F. Ehret for the X-ray work, to Dr. Wm.

(13) Pauling. "Nature of the Chemical Bond." Cornell University Press. Ithaca. N. Y., 1939. pp. 183–84. 270–272. 300–314.

(14) Thompson. THIS JOURNAL. 61. 1396 (1939).

West for the use of the spectrograph. to Dr. Raymond L. Garman and Dr. Marcel E. Droz for the microphotometer curves, and to Mr. D. Rigakos for the micro-analyses.

Summary

The two forms of glucononitrile, A and B, melting at 145 and 120.5°, respectively, shown by earlier work to differ in their optical activity, exhibited, within the accuracy of the measurements, the same X-ray powder diffraction spectra, but different ultraviolet absorption spectra. Aqueous solutions of the B form displayed an absorption band at 2780 Å. and an extinction coefficient given by log ϵ_{molar} = 0.9, approximately. The (ultraviolet) spectrum also underwent complex changes with time. The A form gave a spectrum resembling that of β-hydroxy-propionitrile and showing no absorption maximum at λ 2780 Å. Several cyclic compounds containing carbonyl or imino groups, derivable from the nitrile, are regarded as causing the band at 2780 Å. Interconversion of these compounds may be responsible for the changes with time in the details of the characteristic band, and for the changes in optical rotation as well as for other spectral changes in the short wave ultraviolet. A gradual hydrolysis of the B form would not account for some facts and degradation by loss of hydrogen cyanide was shown to be inconsiderable. Consideration was given to the possibility that the two crystalline forms A and B differed in the nature of the hydrogen bonding.

# Hydration of Unsaturated Compounds.   XI.   Acrolein and Acrylic Acid[1]

BY D. PRESSMAN AND H. J. LUCAS

Kinetics.—The hydration of acrolein[2] is shown by Eq. 1. That of acrylic acid[3] is similar.

(1) Previous communication. X. THIS JOURNAL. 64, 1122 (1942).

(2) J. U. Nef has shown that acrolein undergoes hydration in hot aqueous solution to form hydracrolein. *Ann.,* 335. 219 (1904). Hydration of acrolein in aqueous sulfuric acid can explain the results of Lobry de Bruyn. who isolated a colorless syrup. probably hydracrolein. from a dilute aqueous sulfuric acid solution of acrolein. *Rec. trav. chim.,* 4. 232 (1885).

(3) Acrylic acid undergoes hydration in aqueous sodium hydroxide. E. Lennemann. *Ber.,* 8. 1095 (1875); E. Erlenmeyer. *Ann.,* 191. 281 (1878). Hydracrylic acid undergoes dehydration in 50% sulfuric acid. W. Moldenhauer. *ibid.,* 131. 335 (1864); J. Wislicenus. *ibid.,* 166. 23 (1873).

$$H_2C{=}CHCHO + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HOCH_2{-}CH_2CHO \quad (1)$$
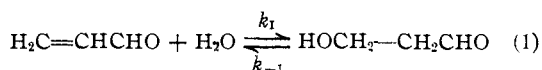
At a given hydronium ion concentration in dilute aqueous solution, the hydration is first order with respect to the unsaturated compound and the dehydration is first order with respect to the hydrated compound, as shown by the straight line character of the plots of $\log_{10} \epsilon/(\epsilon - x)$ against t (Fig. 1), which is the case of two first order reac-