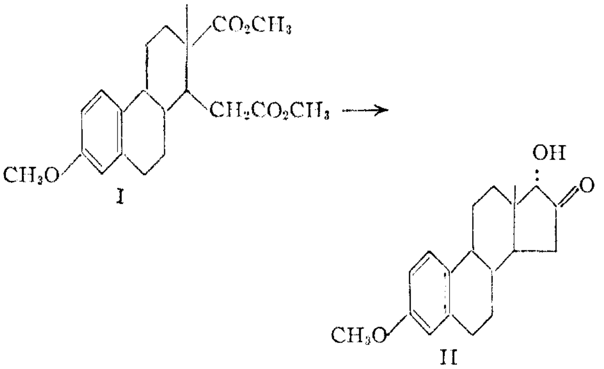
efficient method of forming five- and six-membered rings. Sodium in liquid ammonia has not previously been considered to lead to practical yields of acyloins from esters.[1]

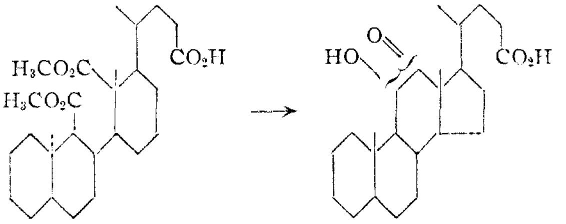
To a solution of 0.8 g. of sodium in 325 ml. of anhydrous ammonia and 225 ml. of ether (under pre-purified nitrogen) was added in one hour 1.8 g. of dimethyl marrianolate methyl ether (I)[2,3] dissolved in 225 ml. of ether. After complete removal of the ammonia by evaporation, the mixture was acidified with hydrochloric acid. Purification afforded 0.890 g. (60%) of 16-keto-α-estradiol-3-methyl ether (II), m.p. 162.0–162.4°, $[\alpha]^{31}_D$ −88° (c = 1.0, 95% ethanol). *Anal.* Calcd. for $C_{19}H_{24}O_3$: C, 75.97; H, 8.05. Found: C, 75.79; H, 8.09. Conventional heterogeneous acyloin reaction conditions (*e.g.*, finely dispersed sodium in refluxing xylene) did not yield detectable quantities of acyloin product from I.

The acyloin II and II acetate showed a depression of m.p. on admixture with 16-keto-β-estradiol-3-methyl ether[4] and the corresponding acetate, respectively. Reduction of II acetate by the ethanedithiol-Raney nickel method,[5] followed by saponification and chromic acid oxidation, afforded estrone methyl ether, identified by comparison with an authentic sample.



I

II



III

IV

By the same technique, 11,12-seco-cholane-24-acid-11,12 dimethyl ester (III) was cyclized in 75–80% yield to an 11,12-acyloin (m.p. 142–143°), identical with the lower melting ketol prepared by Reichstein's procedure[6] (bromination of 12-ketocholanic acid and subsequent alkaline hydrolysis). The non-crystalline diester III was obtained by nitric acid oxidation of 12-hydroxycholanic acid or by chromic acid oxidation of an 11,12-acyloin mixture to 11,12-seco-cholane-11,12,24-triacid[7,8] (m.p. 259–261°), followed by esterification with diazomethane and selective saponification. *Anal.* Calcd. for $C_{26}H_{42}O_6$: C, 69.30; H, 9.40; neut. equiv., 450. Found: C, 69.28; H, 9.25; neut. equiv., 446.

In other experiments employing a ratio of four equivalents of sodium to one of the diesters, the consumption of sodium appeared to be instantaneous. In each series only one of the four possible isomeric acyloins was obtained.

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[1] E. Chablay, *Ann. chim.*, (9) **8**, 205 (1917), was unable to isolate any acyloin material from such a reaction, and M. S. Kharasch, E. Sternfield and F. R. Mayo, *J. Org. Chem.*, **5**, 362 (1940), found the yield of linear acyloin to be much lower than in the case of the heterogeneous reaction.

[2] J. Heer, J. R. Billeter and K. Miescher, *Helv. Chim. Acta.*, **28**, 991 (1945).

[3] W. S. Johnson and R. G. Christiansen, THIS JOURNAL, **73**, 5511 (1951).

[4] M. Huffman and M. H. Lott, *J. Biol. Chem.*, **169**, 167 (1947).

[5] H. Hauptmann, THIS JOURNAL, **69**, 562 (1947).

[6] J. Barnett and T. Reichstein, *Helv. Chim. Acta.*, **21**, 926 (1938).

[7] H. Wieland and P. Weyland, *Z. physiol. Chem.*, **110**, 141 (1920).

[8] H. B. Alther and T. Reichstein, *Helv. Chim. Acta.*, **25**, 816 (1942).

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CRYSTAL STRUCTURE OF CYANURIC ACID

Sir:

The infrared spectra of cyanuric acid and deuterocyanuric acid, which were recently published in THIS JOURNAL, by Newman and Badger,[1] create doubts concerning the values of the interatomic distances found in an early X-ray structure determination by Moerman and Wiebenga.[2]

The crystal structure of cyanuric acid was reinvestigated in our laboratory by G. A. Croes, A. J. van Gent, R. P. van Oosten and D. W. Smits about two years ago. They started from new accurate measurements of the intensities of all X-ray reflections and refined the atomic coördinates by three dimensional Fourier syntheses. This work is not yet published, because we still want to study certain details of the electron density distribution. In connection with Newman and Badger's work, however, it may be interesting to report here the new values for the bond lengths. These are subject to a standard deviation of approximately 0.02 Å., which means that the probability that a given bond length is in error by more than 0.04 Å., or a bond angle by more than 3° is approximately 5%.

The molecules are all planar and situated almost exactly in parallel sheets (101). The old and new interatomic distances and bond angles are shown in Fig. 1 and Fig. 2, respectively, which show one molecule and its connections to others in the same layer.

The deviation from a trigonal symmetry of the central ring (Fig. 1) has disappeared (Fig. 2); the C–N bond lengths in the ring have practically not changed and are still all essentially identical.

On the other hand, a striking difference is observed between the new C=O distances and those previously reported. In the previous structure determination, which was based on estimated intensities and the use of the trial and error method only, we found two different C=O distances (1.24 Å. and 1.31 Å.), each with an estimated probable error of 0.06 Å., so that the difference was not

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[1] R. Newman and R. M. Badger, THIS JOURNAL, **74**, 3545 (1952).

[2] E. H. Wiebenga and N. F. Moerman, *Z. Krist.*, **99**, 217 (1938).

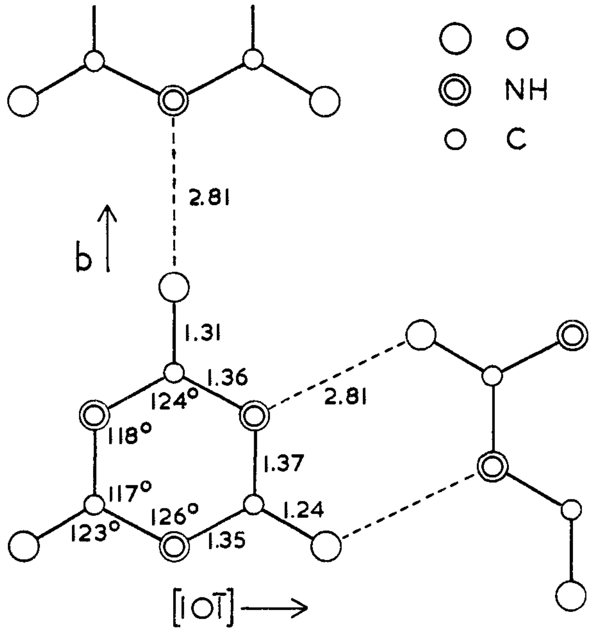

Fig. 1.—Part of crystal structure of cyanuric acid. Hydrogen bonds are indicated by dashed lines; atomic coördinates 1938.[2]

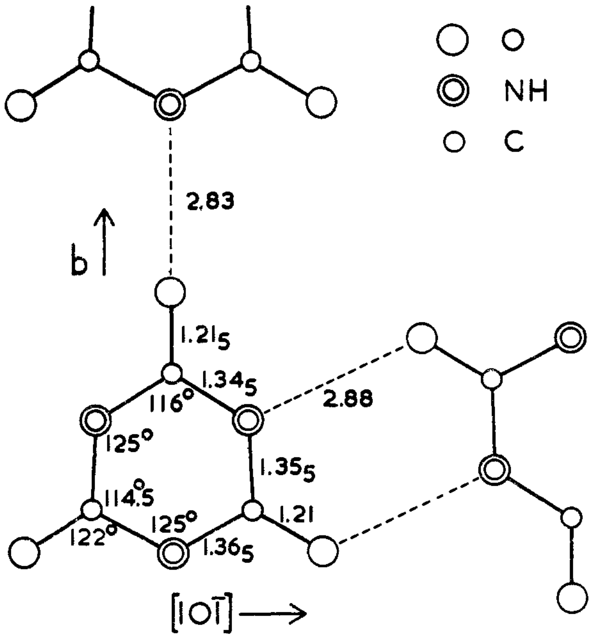

Fig. 2.—As Fig. 1, but with the atomic coördinates taken from a reinvestigation (1950) of the structure.

considered to be significant. The recent investigation proves that the two bonds have essentially the same lengths (1.21 Å. and 1.21_5 Å., respectively), which is in agreement with Newman and Badger's prediction on the basis of the infrared spectra. The new bond length, however, is much smaller than the mean value (1.28 Å.) of those previously observed. It is significantly smaller than the value (1.29 Å.) which is expected from mesomerism between the usually accepted resonating structures, with standard lengths 1.47, 1.26_5, 1.43 and 1.21_5 Å. for the pure C–N, C=N, C–O and C=O bond, respectively. It may be remarked, that small values for the length of a resonating C=O bond are also observed in other carefully investigated structures, namely, 1.19 Å. in N-acetylglycine[3] and 1.21 Å. in *dl*-alanine[4].

Two kinds of hydrogen bonds NH....O connect a molecule with others in the same plane. The first type, designated as class A by Newman and Badger, is directed parallel to the *b*-axis of the crystal; the second, class B, connects the molecules in the [101] direction. In class A the NH bond is directed exactly toward the hydrogen-bonded oxygen, in class B this is almost exactly the case. In our opinion, however, it is not possible to predict with certainty which of the two bonds is the shorter, without taking into account the complicated interaction of a molecule with all neighboring atoms. As is seen from Fig. 2 we find that hydrogen bond A is smaller than 2.85 Å. and possibly significantly shorter than bond B. This would be in disagreement with Newman and Badger's interpretation of the infrared spectra.

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(3) G. B. Carpenter and J. Donohue, THIS JOURNAL, **72**, 2315 (1950).

(4) H. A. Levy and R. B. Corey, *ibid.*, **63**, 2095 (1941); J. Donohue, *ibid.*, **72**, 949 (1950).