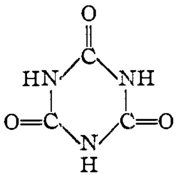
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

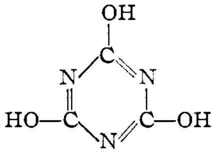
# Absorption Spectra and Tautomerism of Cyanuric Acid, Melamine and Some Related Compounds

BY IRVING M. KLOTZ AND THEMIS ASKOUNIS

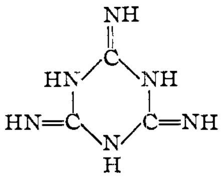
The structures of the six-membered heterocyclic rings which occur in cyanuric acid and related compounds have been the subject of much interest,[1-5] particularly in the cases of the highly symmetrical molecules where strong resonance is possible. The structures of cyanuric acid and melamine in the solid state have been worked out clearly from X-ray investigations, and have been found to be represented best by the resonance configurations of the carbonyl form (I) in the former case, and by the resonance hybrid of the amide form (IV) in the latter molecule.



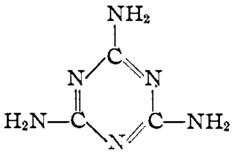
(I)



(II)



(III)



(IV)

In aqueous solution, however, the nature of cyanuric acid has been the subject of much discussion.[1,3] For both cyanuric acid and melamine the situation in solution may be complicated by the existence of tautomeric equilibria. Under these circumstances, conclusions as to structure based on chemical behavior are open to question, since a tautomeric equilibrium may be shifted to the less prevalent form if the latter reacts more rapidly than the predominant form. Consequently an investigation was undertaken of the absorption of ultraviolet radiation in aqueous solutions of these heterocyclic compounds in order to study any tautomeric equilibria without simultaneously affecting them. The results obtained indicate that the forms in neutral solution are the same as those in the solid state, but that acid or base causes some structural modifications.

## Experimental

**Reagents.**—All the cyanuric derivatives were kindly supplied by the American Cyanamid Company. The cyanuric acid had been re-precipitated twice by the use of alkali and acid, and the melamine was 99.7% pure when received. Cyanuric chloride was purified by recrystallization from chloroform. The urea was a sample of reagent grade. Solutions of guanidine hydrochloride were prepared by dissolving a weighed quantity of guanidine carbonate, previously recrystallized twice from water–ethanol mixtures, in a solution of hydrochloric acid. The recrystallized materials were dried in a vacuum desiccator with the aid of an oil pump and a carbon dioxide–acetone trap. The diethyl barbituric acid was of U. S. P. grade.

**Spectral Measurements.**—Ultraviolet absorption spectra were measured with the Beckman quartz spectrophotometer, using 1 cm. silica cells. Extinction coefficients were calculated from the familiar equation

$$\epsilon = 1/cd \log_{10} (I_0/I)$$

where $I_0$ is the intensity of the light passing through the solvent, $I$, the intensity of the light passing through the solution, $c$, the concentration of the solute in moles per liter, and $d$, the thickness of the cell in centimeters.

## Results and Discussion

The ultraviolet absorption spectra of cyanuric acid in aqueous solution at various *p*H's are summarized in Fig. 1. Clearly the addition of base progressively changes the cyanuric acid from a non-absorbing form to a strongly absorbing molecule. The very low absorption of the form that predominates in acid solution indicates the presence of structure (I) with some resonance contribution from configurations involving a separation of charge and ring conjugation. The spectrum of the carbonyl form is similar to that of urea (Fig. 4) in general shape, though the magnitude of the extinction coefficients of the former is somewhat larger than that of the latter.

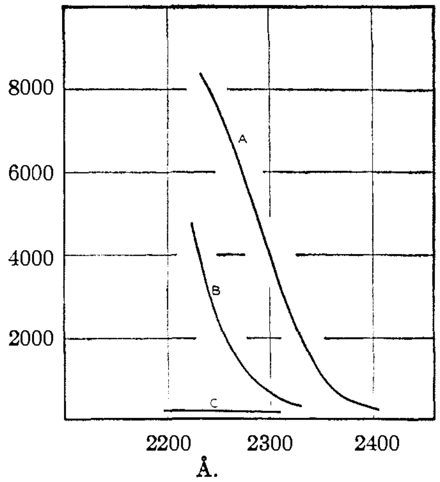


Fig. 1.—Absorption spectra of cyanuric acid: **A**, 0.10 *N* NaOH; B, *p*H 7.93; C, *p*H 0.87.

In basic solution, the absorption of radiation is quite high (Fig. 1). While the absorption peak is

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(1) E. Agallidis, H. Fromherz and A. Hartmann, *Ber.*, **71**, 1391 (1938).

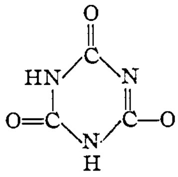
(2) E. H. Wiebenga and N. F. Moermann, *Z. Krist.*, **99**, 217 (1938).

(3) H. Biltz, *Ber.*, **72**, 807 (1939).

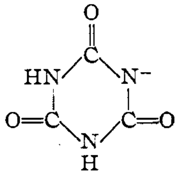
(4) I. E. Knaggs and K. Lonsdale, *Proc. Roy. Soc.*, (*London*), **A177**, 140 (1940).

(5) E. W. Hughes, THIS JOURNAL, **63**, 1737 (1941).

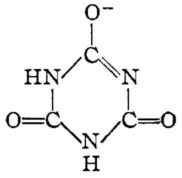
slightly beyond the limit of the present spectrophotometer, there is strong indication of a maximum just below 2200 Å., in agreement with earlier investigations.[1] Nevertheless, the presence of a maximum so far toward the short wave length region of the ultraviolet would argue against the presence in basic solution of a structure such as (II). On the other hand, since cyanuric acid must exist as an anion in basic solution, resonance between the following ionic forms may occur in addition to that obtained in the neutral molecule (I)



(V)



(VI)



(VII)

Resonance in such a system gives rise to a structure which may reasonably be the ground state in a transition corresponding to the absorption of radiation near 2200 Å.

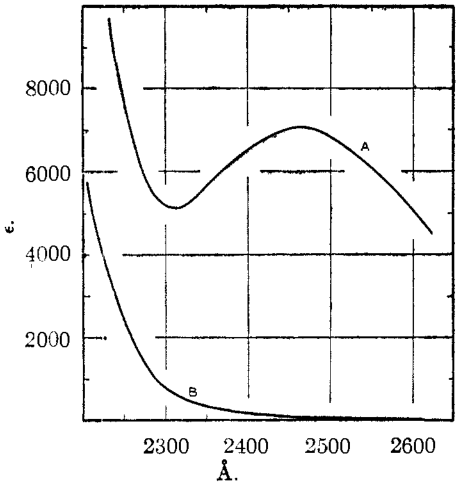
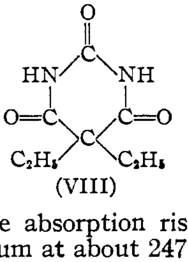


Fig. 2.—Absorption spectra of barbital: A, 0.10 $N$ NaOH; B, $p$H 1.16.

This interpretation seems to be substantiated by the behavior of diethylbarbituric acid at various $p$H's. Again, in acid solution the absorption is quite weak and only at the far end of the ultraviolet (Fig. 2) as would be expected from the resonance hybrid of the carbonyl form (VIII). In



(VIII)

basic solution the absorption rises strongly and exhibits a maximum at about 2470 Å. Since barbital, like cyanuric acid, is acidic it too must exist as an anion in basic solution, and hence the strongly absorbing form must have a structure analogous to configurations (V) to (VII). The difference in wave lengths of the maxima of barbital and cyanuric acid may be attributed to a greater contribution of resonance configurations involving charge separations and triple conjugation to the structure of the former substance.

The ultraviolet absorption spectra of melamine as a function of $p$H, in aqueous solution, are illustrated in Fig. 3. In contrast to cyanuric acid,

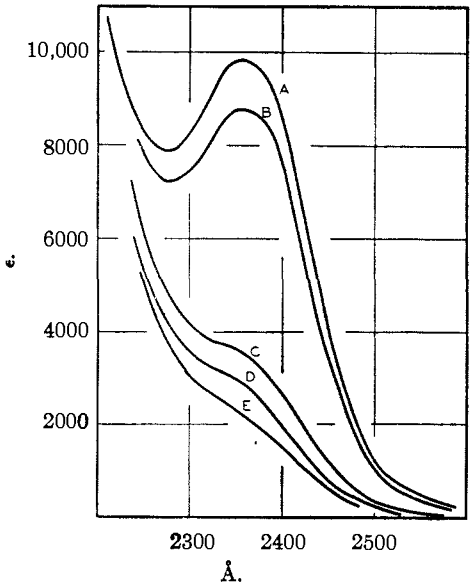
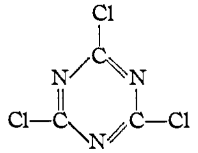


Fig. 3.—Absorption spectra of melamine: A, $p$H 1.01, 1.65, 2.83; B, $p$H 4.23; C, $p$H 5.58; D, $p$H 6.25; E, $p$H 7.03, 10.77.

the spectrum of melamine is strong in acid solution, but analogous to the situation with cyanuric acid is the progressive change in spectrum with $p$H. The absorption peak at 2360 Å. in acid solution is quite close to that of cyanuric chloride (Fig. 4).

Cyanuric chloride is structurally incapable of undergoing tautomeric shifts and hence must exist predominantly in a configuration of the form

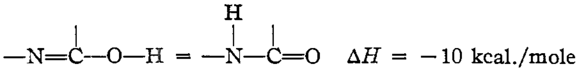


(IX)

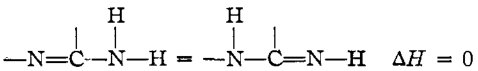
Since melamine in acid solution exhibits a peak near that of cyanuric chloride, the amide form (IV) seems most reasonable for this compound. Furthermore, since the spectra in neutral and basic solution also show a vestige of the 2360 Å. band, though of much reduced intensity, structure (IV) would also seem most likely under these conditions. The increase in absorption intensity on addition of acid may be attributed to the binding of a hydrogen ion with consequent formation of a cation and the destruction of the symmetry of the neutral molecule. The reduced symmetry, by increasing the dipole strength, would increase the transition probability and hence the intensity of absorption.

It is of interest to note in passing that the acid $pK$ of the melamine cation as determined from spectral variations (5.05) agrees well with the value calculated from direct titration experiments with a glass electrode (5.10).

Absorption spectra thus indicate that the most stable forms of cyanuric acid and melamine, respectively, in neutral aqueous solution are essentially the same as those in the solid state. It is of interest to observe that in both states, the carbonyl form (I) is the more stable structure for cyanuric acid, whereas the amide structure (IV) is the more stable for melamine. The basis of this difference is apparent when one considers the relative energies involved. Branch and Calvin[6] have pointed out that the transfer of a hydrogen atom is favored much more in enol-keto tautomerism than in amide-imide conversions, *i. e.*,



$$—N{=}\overset{|}{C}—O—H = —\overset{\overset{H}{|}}{N}—\overset{|}{C}{=}O \quad \Delta H = -10 \text{ kcal./mole}$$



$$—N{=}\overset{|}{C}—\overset{\overset{H}{|}}{N}—H = —\overset{\overset{H}{|}}{N}—\overset{|}{C}{=}N—H \quad \Delta H = 0$$

Thus in cyanuric acid, the keto formation is accompanied by a stabilization energy of 30 kilocalories/mole which is more than sufficient to overbalance the extra resonance energy which would be obtained from the conjugation within the ring in the enol form. In contrast in melamine, the conversion from the amide to the imide form merely trades one C=N for another and produces no net stabilization energy. In consequence the additional resonance energy obtained by conjugation within the ring is more than sufficient to stabilize the molecule in the amide form.

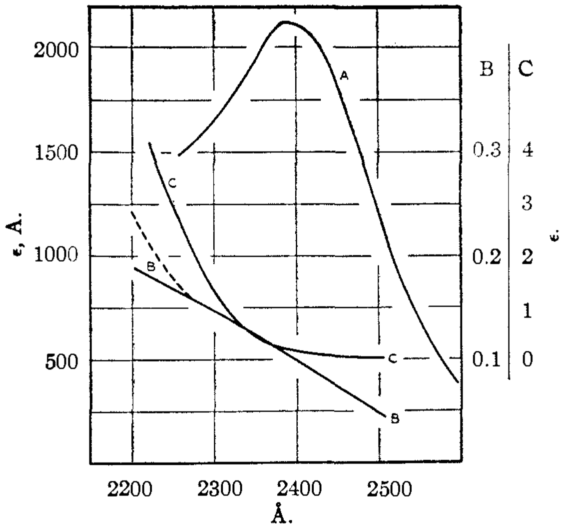


Fig. 4.—Absorption spectra of: A, cyanuric chloride in methyl alcohol; B, guanidine, —, $p$H 1.04, ----, $p$H 6.24; C, urea in 0.10 $N$ NaOH.

## Summary

The absorption spectra of cyanuric acid, melamine, cyanuric chloride, barbital, guanidine, and urea have been investigated in aqueous solutions at various $p$H's. From these observations it is concluded that cyanuric acid exists in the carbonyl form and melamine in the amide configuration in neutral solution, but that acid or base causes modifications in structure.

EVANSTON, ILLINOIS RECEIVED OCTOBER 28, 1946

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(6) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 289.

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[CONTRIBUTION FROM DOW CORNING CORPORATION]

# Organosilicon Polymers. III. Infrared Spectra of the Methylpolysiloxanes

BY NORMAN WRIGHT[1] AND MELVIN J. HUNTER[2]

In the study of a new class of compounds the infrared absorption spectra rank high in importance since these spectra are unquestionably among the most distinguishing of the physical properties of molecular substances. The frequencies of vibration and the absorption intensities depend directly upon the masses of the atoms, the strengths and electrical characters of the interatomic bonds, and the geometrical configuration of the molecule; hence, interpretation of the spectra often leads to fundamental information on molecular structure. Treated solely from an empirical point of view, the spectra are of considerable value for identification and quantitative analysis.

Literature reports on infrared spectra of silicon containing compounds include studies of silane,[3,4] halosilanes,[5,6] carborundum,[7] and a large number

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(1) The Dow Chemical Company, Midland, Michigan.

(2) Dow Corning Corporation, Midland, Michigan.

(3) W. B. Steward and H. H. Nielsen, *J. Chem. Phys.*, **2**, 712 (1934); *Phys. Rev.*, **47**, 828 (1935).

(4) C. H. Tindal, J. W. Straley and H. H. Nielsen, *Proc. Natl. Acad. Sci. U. S.*, **27**, 208 (1941); *Phys. Rev.*, **62**, 151 (1942).

(5) C. R. Bailey, J. B. Hale and H. W. Thompson, *Proc. Roy. Soc.* (London), **167**, 555 (1933).

(6) Clemens Schaefer, *Z. Physik*, **60**, 586 (1930).

(7) W. W. Coblentz, Publication No. 65, Carnegie Inst. of Wash. (1906).