droxy groups. Like the alcohols,[18] monostearin and distearin have an ϵ_∞(arc) considerably larger than ϵ_∞(calcd.), indicating the possibility of another dispersion region. Of the three stearins, monostearin, possessing two hydroxyl groups to give rise to hydrogen bonding, has the longest

(18) G. B. Rathmann, A. J. Curtis, P. L. McGeer and C. P. Smyth, to be published.

critical wave length at 80°. Distearin, which is of intermediate molecular size with only one hydrogen bonded group, has the smallest critical wave length of the three, and the unassociated tristearin, which has much the largest molecule of the three, has a critical wave length slightly larger than that of distearin.

PRINCETON, NEW JERSEY

Infrared Spectra of Cyanuric Acid and Deutero Cyanuric Acid[1]

BY ROGER NEWMAN AND RICHARD M. BADGER

The infrared spectra of sublimed films of cyanuric acid and deutero cyanuric acid, and the polarized spectra of (101) single crystals of cyanuric acid are reported. The active valence fundamentals and the higher frequency bending vibrations have been identified. A characteristic feature of the spectrum is the occurrence of several doublet bands which represent pairs of vibrations whose degeneracy is removed in the potential field of the crystal. The splitting of the carbonyl frequency is very small which is taken to indicate the near equivalence of all C=O bonds in the molecule. The splitting of N–H valence vibrations is large indicating the presence of two considerably different hydrogen bonds. These results are in disagreement with the X-ray structure determination of Wiebenga and Moerman, which is believed to be in some error.

Introduction

Crystalline cyanuric acid, $(HNCO)_3$, is of spectroscopic interest for several reasons. An X-ray examination[2] has indicated that the crystal contains two slightly different types of N–H···O hydrogen bond, both of which are among the shortest which have so far been reported. A study of this substance may consequently be expected to contribute to our knowledge regarding the hydrogen bonding of amides which until the present is very limited. A comparison of the spectrum with that of diketopiperazine,[3,4] with which it has much in common, should be particularly interesting. The simplicity and high symmetry of the cyanuric acid molecule leads to the expectation that a reasonably unique analysis of the spectrum should be possible, at least as regards the more important features.

Figure 1 presents a section of the unit cell of cyanuric acid. The internuclear distances, for which we are indebted to Dr. R. A. Pasternak, were recalculated from the X-ray data of Wiebenga and Moerman.[1] As is readily seen the molecules are tied together by hydrogen bonds in parallel sheets. These bonds are of two classes, which we shall designate as A and B, and differ in the direction of approach of the hydrogen atom to the oxygen which it links to nitrogen. In class A, there is a "head on" approach. The line connecting the N and O atoms is parallel to the C=O bond, and incidentally to the b axis of the crystal. In class B the angle between C=O and N···O directions is about 124°. In both cases the N···O distance was reported to be about 2.81 Å., though from the direction of approach to the oxygen one

might have expected the B hydrogen bonds to be the stronger.

The central ring of the molecule is planar; the C–N bonds appear to be all essentially identical and from their distance appear to have approximately 50% double bond character. One should consequently expect the ring frequencies to follow rather closely the pattern of an isolated D_{3h} cyanuric acid molecule though in the crystal the molecules actually lie at sites of only C_2 symmetry. In the peripheral vibrations, on the other hand, one might anticipate more obvious effects of the reduced symmetry, both in a splitting of frequencies and in the selection rules. However, since the interactions between molecules in any one of the (101) planes is presumably much greater than those between molecules in adjacent planes, the characteristics of a C_{2v} molecule might well be retained in the spectrum to a considerable degree.

Some results of the X-ray investigation appear rather anomalous, in particular the two considerably different C=O distances. If the parameters are to be taken at face value, one should expect the C=O frequency to appear as a wide doublet. The high frequency component, polarized in the [10$\bar{1}$] direction, should have a frequency around 1710 cm.$^{-1}$ as in diketopiperazine, but a qualitative application of Badger's rule as well as a comparison with other molecules suggests that the component polarized parallel to the b axis should have a frequency about 150–200 cm.$^{-1}$ lower. The longer C=O distance might well be a symptom that the A class hydrogen bonds are the stronger, though this is not reflected in the N···O distances reported, and as mentioned above is contrary to expectation.

Experimental

Single crystals of cyanuric acid were prepared by sublimation of the Eastman Kodak Co. (white label) reagent. The sublimation was carried out at about 120° in sealed evacuated glass tubes. The crystals grew as small (101)

(1) This research was supported by the Office of Naval Research under Contract N6-ori-102, V1.

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

(3) R. Newman and R. M. Badger, J. Chem. Phys., 19, 1147 (1951).

(4) E. J. Ambrose, A. Elliott and R. B. Temple, Proc. Roy. Soc. (London), 206A, 192 (1951).
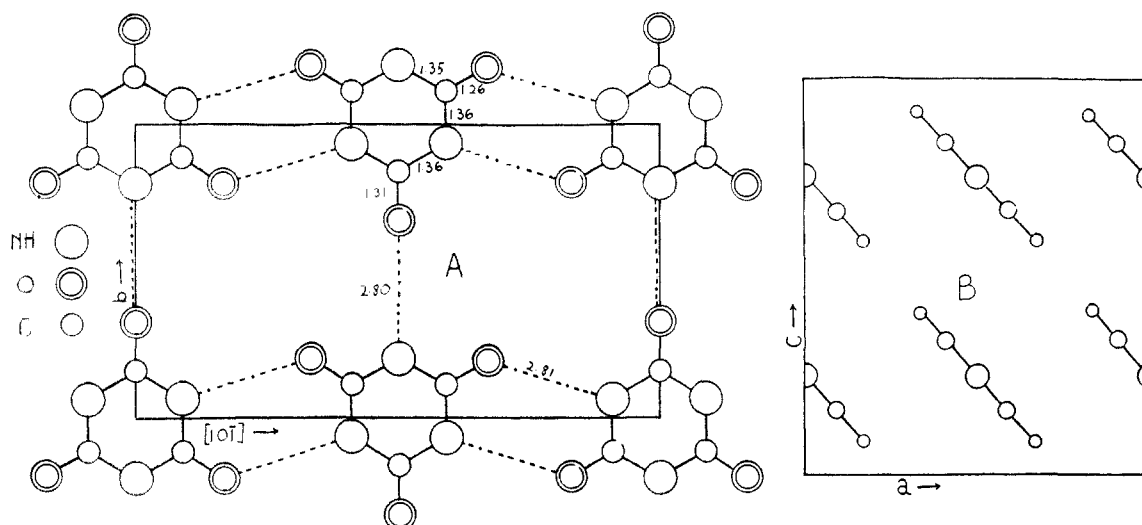
Fig. 1.—The unit cell of cyanuric acid. Fig. A shows a typical (101) net. Fig. B is a (010) projection. Hydrogen bonds are indicated by dashed lines. The distances shown were recalculated from the data of Wiebenga and Moerman.

plates[5] of the order of 1 mm. on an edge and ranging in thickness from about 2 or 3 μ to about 50 μ. Identification of axes was made optically and was checked by X-ray methods. The crystals were mounted for use with our infrared microilluminator.[6] The powder films employed in this study were prepared by vacuum sublimation onto AgCl plates. Partially deuterated cyanuric acid was prepared by allowing the ordinary material to stand for 24–48 hours with an excess of D_2O. Spectra were taken with a vacuum grating instrument[7] in the range from 3600 to 2700 cm.$^{-1}$, with a Beckman IR-2 spectrometer in the range from 3500 to 667 cm.$^{-1}$ and with a KBr prism instrument[8] from 790 to 450 cm.$^{-1}$. A silver chloride polarizer[9,10] was used.

Results and Discussion

As mentioned above the disposition of the molecules in the crystal lattice would indicate that an analysis of the vibrations in terms of a molecule having effective C_{2v} symmetry would probably provide an adequate approximation to the grosser features of the observed spectrum. Two features of practical interest mark the breakdown of symmetry from D_{3h} to C_{2v}. First, the totally symmetric infrared inactive species of $D_{3h}(A_1')$ can pass into an active species of $C_{2v}(A_1)$. Second, the double degeneracies are destroyed. In particular, the vibrations comprising a given in-plane degenerate pair (species E') are resolved into two components, one active parallel and the other perpendicular to the C_2 axis. If the intermolecular perturbations are not too great, the formerly degenerate pair would appear in the spectrum as a doublet, the two components of which should have mutually perpendicular polarization.

(5) X-Ray photographs of a crystal plate of somewhat inferior optical quality showed it to consist of crystals whose (101) planes had a common b direction but which were rotated about this direction by small angles from the nominal (101) plane, *i.e.*, the surface of the plate. The angular dispersion is probably smaller in the crystals employed for the spectroscopic work though, in any event, the effect on the observed spectrum would be quite negligible.

(6) R. M. Badger and R. Newman, *Rev. Sci. Instruments*, **22**, 935 (1951).

(7) R. M. Badger, L. R. Zumwalt and P. A. Giguère, *ibid.*, **19**, 861 (1948).

(8) A gift of the Shell Development Company.

(9) R. Newman and R. S. Halford, *Rev. Sci. Instruments*, **19**, 270 (1948).

(10) N. Wright, *J. Optical Soc. Am.*, **38**, 69 (1948).

In Fig. 2 we have shown the polarized spectra of a (101) crystal plate and of a spectrum of a sublimed film of the partially deuterated material. In the latter the bands which appear only upon deuteration are shown as dashed curves. In Table I the observed frequencies are listed together with the proposed assignments. Though a complete analysis is not possible with our data, it has been possible to identify the active valence vibrations and the higher frequency bending modes.

TABLE I

FREQUENCIES (CM.$^{-1}$) OBSERVED FOR CYANURIC ACID

[010]	[10Ī]	Out of plane[a]	In-tensity	Assignment
3210 >> 3210			s	Degenerate N–H stretch
3060 << 3060				
	2960	...	ms	
	2900	...	ms	
2530	2530	?	w	
2150	2150	?	w	
1800 >	1800		ms	sym C=O stretch
1710 =	1710		vs	Degenerate C=O stretch
1470 =	1470		s	Degenerate in-plane ring stretch
1425	1410		ms	Degenerate N–H in-plane bend
1065	1050		ms	Degenerate in-plane ring stretch
..		853	w	
..		807	w	N–H out of plane bend (?)
		765	w	C=O out of plane bend (?)
	744		w	
695			ms	
545	535		vs	Degenerate C=O in-plane bend

[a] Bands, which appear stronger in the spectrum of a powdered specimen than in that of a single crystal of equivalent thickness, are characterized as out of plane. The new frequencies which appear upon deuteration occur at 2410, 2310, 885–875, and 570 cm.$^{-1}$.

Hydrogen Frequencies.—The pair of perpendicularly polarized frequencies at 3210 and 3060 cm.$^{-1}$, have been assigned to the degenerate N–H
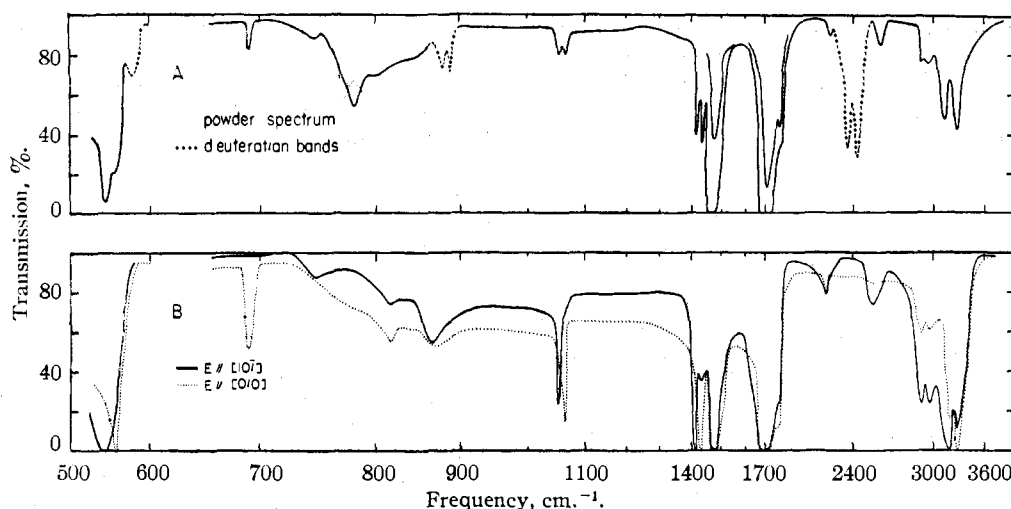
Fig. 2.—Infrared spectra of cyanuric acid. Fig. A shows the spectrum of a sublimed film of a 50-60% deuterated sample. The dashed curves show the bands which appear on deuteration. The dotted curves are sections of the spectrum of a sublimed film of the ordinary substance. The thickness is approximately equal for the two samples. Fig. B shows the polarized spectra of a (101) crystal.

stretching vibrations. In the deuterated compound they are shifted to 2410 and 2310 cm.$^{-1}$, respectively. The comparative sharpness of these bands is surprising in view of the very short hydrogen bond distances indicated by the X-ray investigation, since a strong coupling with lattice vibrations might well be anticipated. Furthermore, the frequencies seem rather high, particularly that of the 3210 cm.$^{-1}$ component which is polarized parallel to the b axis. In diketopiperazine, with N···O hydrogen bond distance of 2.85 Å., a very broad absorption region was observed with maximum at about 3000 cm.$^{-1}$. For these reasons, as well as for others given below, it is very probable that the N···O distance parallel to the b axis in cyanuric acid was considerably underestimated by Wiebenga and Moerman.

The bands at 2960 and 2900 cm.$^{-1}$ appearing as shoulders on the N–H doublet have been somewhat troublesome. Though the N–H symmetric stretch might be expected to appear weakly in this region it is unlikely that either band is attributable to this vibration. The symmetric stretch should be active along [010], but for the bands in question I([10$\bar{1}$]) << I([010]). Furthermore no shifted band of comparable intensity is found in the spectrum of the partially deuterated compound, though this spectrum has been observed under conditions such that the 2410 and 2310 cm.$^{-1}$ bands were considerably more intense than their 3210 and 3060 cm.$^{-1}$ counterparts (see Fig. 1A). The weak band at 2150 cm.$^{-1}$ is unaffected by deuteration. It consequently seems necessary to attribute 2960 and 2900 cm.$^{-1}$ to combination or overtones. One of them is very plausibly assigned to 2 × 1470, but the interpretation of its companion is more difficult. It is possible that 3 × 1050 is not excluded and a combination of the unidentified inactive ring frequency with one of the active carbonyl or ring frequencies may also be considered.

From the polarization behavior the 2960 and 2900 cm.$^{-1}$ bands appear to involve levels of the same symmetry types as the adjoining N–H stretch

and may well borrow intensity from the latter, provided there is sufficient interaction between the respective vibrations. From a consideration of the resonating structures contributing to the ground state of the amides a very considerable interaction between the N–H stretch and both carbonyl and C–N vibrations should be expected.

The assignment of the doublet at 1410 and 1425 cm.$^{-1}$ to the "degenerate" in-plane N–H bending modes is supported by the mutually perpendicular polarization and by the shift to 885 and 875 cm.$^{-1}$ on deuteration. This assignment is further in qualitative agreement with the Teller–Redlich product rule.[11] The fact that the higher frequency component is polarized parallel to the b axis of the crystal possibly supports the belief that the B class hydrogen bonds are the stronger. The narrowness of the bands is again rather surprising.

Carbonyl Frequencies.—The predictions based on the X-ray data previously discussed have not been verified. The intense band at 1710 cm.$^{-1}$ is rather broad and may very possibly correspond to an unresolved doublet, though the separation can at most correspond to a few frequency units. It appears to be unpolarized, though the observations are not wholly satisfactory owing to excessive absorption in the thinnest crystal obtainable. No frequency was observed which can be attributed to the presence of a C=O group with bond distance of around 1.31 Å. A weak, high frequency shoulder at 1810 cm.$^{-1}$ is polarized parallel to the b axis and can reasonably be ascribed to the symmetrical C=O stretch which would be inactive in the D_3^h molecule.

A very strong band was observed at 540 cm.$^{-1}$ which is apparently a narrow doublet. The frequency and mutually perpendicular polarization of the components suggest that it originates in the in-plane C—O bending vibrations. In urea the analogous vibration lies at 574 cm.$^{-1}$.[12]

(11) ν(N–H stretch) × ν(N–H bend) / ν(N–D stretch) × ν(N–D bend) ≈ 2(theor.) ≈ 2.1 (exp.).

(12) Robert D. Waldron, Ph.D. Thesis, California Institute of Technology, 1951.

Ring Frequencies.—In the isolated D_{3h} cyanuric acid molecule one should expect four ring stretching frequencies, of which two, of symmetry class A_1' and A_2', are inactive in the infrared. Of the two doubly degenerate E' pairs one should probably be quite active and the other only moderately so. If the ring were stripped of peripheral atoms this vibration would become virtually inactive due to the near equality of the masses of nitrogen and carbon atoms. In the reduced symmetry of the crystal, the vibration derived from A_1' might become weakly active, but the A_2' mode should scarcely be expected to gain significant activity. As was mentioned above, the splitting of the E' pairs might well be rather small.

We ascribe the single intense and unpolarized band at 1470 cm.$^{-1}$ to one of these pairs and the perpendicularly polarized narrow doublet at 1050 and 1065 cm.$^{-1}$ to the other. None of these bands shows appreciable shift on deuteration. The last mentioned doublet, however, appears to suffer significant decrease in intensity on deuterium substitution, though our observations are very qualitative. This is perhaps not surprising since for reasons mentioned above one of the E' pairs may owe a considerable portion of its moderate intensity to the small motions of peripheral atoms, the amplitudes of which may be significantly affected by deuteration.

Out of Plane Vibrations.—From their relatively high intensity in the powder spectrum as compared with that of the (101) crystal, it is probable that 807 and 765 cm.$^{-1}$ correspond to out of plane vibrations. The former appears to shift to 570 cm.$^{-1}$ on deuteration ($807/570 = 1.4$), while the latter

both increases in intensity and shifts slightly to higher frequency. The small frequency shift could be accounted for by an interaction between the two vibrations. Presumably the only out of plane fundamentals which could lie in this region are the N–H and C=O bendings. We tentatively ascribe 807 cm.$^{-1}$ to the former, though the frequency seems rather low for this mode, and 765 to the latter. In a previous investigation[8] the out of plane C=O bend in urea was ascribed to 790 cm.$^{-1}$.

Conclusion

As has been shown above the infrared observations are compatible with a previous X-ray structure determination as far as the presence of an essentially symmetrical ring is concerned; but are in disagreement in regard to the periphery of the cyanuric acid molecule. In contradiction to the X-ray determination it appears very probable that all C=O distances are nearly equal and are not greater than the 1.25 Å. found in diketopiperazine. The N–H···O hydrogen bond distances, on the other hand, are probably not all equal. The stronger bond appears to be formed in the case when the C=O and N···O directions make an angle of around 124° with each other. The bonds parallel to the b axis must be lengthened corresponding to the shortening of the C=O distance, and the N–H···O distance is probably not less than 2.87 Å.

PASADENA 4, CALIFORNIA

The Microwave Spectrum and Structure of Methylene Fluoride[1]

BY DAVID R. LIDE, JR.[2]

The K-band microwave spectrum of the slightly asymmetric rotor CH_2F_2 has been recorded and analyzed. Many of the lines appear as close doublets which are due to asymmetry splitting of levels which would be degenerate in the limiting symmetric rotor. The rotational constants determined from the three lines of lowest J values are $a = 49,138.4$ mc.; $b = 10,603.89$ mc.; and $c = 9249.20$ mc. With the aid of two lines of $C^{13}H_2F_2$ the following structural parameters have been calculated: $r_{CF} = 1.358 \pm 0.001$ Å., $r_{CH} = 1.092 \pm 0.003$ Å., $\angle FCF = 108° 17' \pm 6'$, $\angle HCH = 111° 52' \pm 25'$. Stark effect measurements give a dipole moment of 1.96 ± 0.02 debye units.

The structure of methylene fluoride, CH_2F_2, has previously been studied by electron diffraction[3] and by high-resolution infrared spectroscopy,[4] with results in rather poor agreement. The dipole moment has not been reported. The structure of this molecule is of interest in connection with recent radio-frequency and microwave spectroscopic investigations of other halogenated methanes, which have yielded useful information on the nature of the chemical bond.

The available structural information indicated

that CH_2F_2 should be a slightly asymmetric rotor ($\kappa \sim -0.93$) with dipole moment in the axis of intermediate moment of inertia (the C_2 symmetry axis). The magnitude of the reciprocal moments of inertia was such that the only transitions likely to fall below 40,000 mc. would be of the type $\Delta J = +1$, $\Delta K = -1$. (The notation of King, Hainer and Cross[5] will be used, with K understood to mean K_{-1}.) Since transitions of this type are very sensitive to the exact values of the structural parameters, it was impossible to predict with any certainty the transitions which would fall in the accessible frequency region.

A sample of CH_2F_2 was kindly provided by Dr.

(1) The research reported in this paper was made possible by support extended Harvard University by the Office of Naval Research under O.N.R. Contract N5ori-76, Task Order V.

(2) Standard Oil of California Predoctoral Fellow.

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(4) H. B. Stewart and H. H. Nielsen, Phys. Rev., **75**, 640 (1949).

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