Behavior at Higher *p*H Values.—Cobaltous hydroxide precipitates from dilute solutions at *p*H values between 6.8 and 7.5. The color of the hydroxide may be blue, or rose, for X-ray analysis has shown two isomeric forms.[11] A fresh precipitate of the hydroxide is readily oxidized to the brown hydroxide by the air at higher *p*H values. Bovine serum albumin appears to form a soluble complex with cobaltous hydroxide. The characteristic spectrum of Fig. 3 was obtained after forming the complex in a nitrogen atmosphere. When the complex was prepared in air some oxidation of cobalt was indicated by a decrease in optical density above 560 mμ and an increase at lower wave lengths.

Proteins react with cobaltous chloride under the conditions of the biuret reaction to form a violet-red complex which is rapidly oxidized to a brown cobaltic complex.[12] The brown complex has no characteristic absorption maxima in the visible spectrum but shows increasing absorption with decreasing wave length (Fig. 4). When the protein was bovine serum albumin the oxidation occurred in an inert atmosphere as well as in air. By contrast, α-casein formed a stable violet-red complex in a nitrogen atmosphere (Fig. 4), and the typical oxidized solution in air. Since α-casein contains but two cystine units per 10^5 g. of protein, while the same unit of bovine serum albumin contains 22.5 cystine units it appears probable that the disulfide groups may oxidize the cobaltous ion in alkaline solution. Only a fraction of the cobaltous complex is oxidized by α-casein in an inert atmosphere because of the low cystine content.

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WHEATON, ILLINOIS

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Microwave Absorption and Molecular Structure in Liquids. VIII. Dielectric Relaxation in Some Long-Chain Esters[1,2]

BY P. L. MCGEER,[3] A. J. CURTIS, G. B. RATHMANN AND C. P. SMYTH

RECEIVED FEBRUARY 28, 1952

Dielectric constants and losses between 3 and 90° at wave lengths of 1.25, 3.22 and 10.0 cm. and 577 m. have been measured for ethyl, isoamyl, cetyl and octadecyl acetates, tetradecyl palmitate, decyl, tetradecyl and cetyl stearates, tristearin, distearin and monostearin, and ethylene dimyristate, dipalmitate and distearate. Refractive indices, densities and viscosities have also been measured. The critical wave length, at which the loss is a maximum, increases with molecular length and with viscosity, as observed previously for alkyl bromides. The viscosities of the esters are slightly lower than those of alkyl bromides of about the same molecular length, but the critical wave lengths are only about half as large, showing greater ease of dielectric relaxation. Orientation of polar molecular segments, presumably, occurs by rotation around the carbon-carbon bonds.

In previous papers of this series the results of investigations of twenty-seven alkyl bromides and related compounds in the pure state and a number of specially selected systems of organic halides in non-polar solvents have been reported and discussed. The work on the pure polar liquids has provided information on the effects of molecular size and shape upon dielectric relaxation and has served to contrast and compare the processes of dielectric relaxation and viscous flow. In the work on dilute solutions, in which it has been possible to vary the environment of the polar molecules, extreme departures from the classical Debye proportionality between the viscosity and the dielectric relaxation time have been observed. These departures have been attributed to intermolecular forces and the effects of the solvent on differently shaped orienting units. The intermolecular forces have been associated with the interaction between the solute and permanent local, as well as induced, dipoles in the solvent molecules. The present paper, which discusses measurements upon a series of long-chain esters of high viscosity, is a continuation of the work on pure liquids.

Purification of Materials

Table I lists the melting or boiling points, refractive indices, and densities of the compounds studied. The three glycerides, kindly loaned by the Procter and Gamble Company, were used without further purification. The ethylene diesters obtained from the Matheson Co. were used after recrystallizing several times from a benzene-methanol mixture. The ethyl and isoamyl acetates were dried over finely divided potassium carbonate for 24 hours and repeatedly distilled in a 4-foot column. The cetyl and octadecyl acetates, also obtained from the Matheson Co., were subjected to two vacuum distillations and then recrystallized several times from an ether-methanol solvent. The remain-

TABLE I

PHYSICAL CONSTANTS OF MATERIALS

	M.p., °C.	t, °C.	d^t_4	n^t_D
Ethyf acetate	77–77.2	50	0.863	1.37257 (20°)
	(b.p.)	25	.894	
Isoamyl acetate	141.5–141.7	70	.823	1.40169 (18°)
	(b.p.)	27	.866	
Cetyl acetate	18.3	60	.810	1.41846 (80.3°)
		30	.830	
Octadecyl acetate	32.6	60	.830	1.42957
		30	.851	
Decyl stearate	35.4	80	.8423	1.42967
Tetradecyl palmitate	46.4	80		1.42987
Tetradecyl stearate	50.1	80		1.43279
Cetyl stearate	56.8	80	.816	1.43400
		60	.829	
Monostearin	72.4	90		1.43963
Distearin	76.7–77.5	90		1.43771
Tristearin		90		1.43711
Ethylene dimyristate	61.7	80	.8600	1.43168
Ethylene dipalmitate	69.1			
Ethylene distearate	75.3			

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[1] This research has been supported in part by the Office of Naval Research. Reproduction, translation, publication, use or disposal in whole or in part by or for the United States Government is permitted.

[2] This paper represents a part of the work submitted by Dr. P. L. McGeer to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] Ethyl Corporation Fellow in Chemistry, 1949–1950; McCay Fellow in Chemistry, 1950–1951.

ing four compounds were synthesized and purified by Dr. R. W. Crowe[4] in this Laboratory.

Experimental Results

The experimental method for measuring dielectric constant and loss at 1.25 and 3.22 cm. has been reported in other papers of this series.[5-7] The measurements in the 10-cm. region were made with a short-circuited coaxial slotted line cell,[8] and the effectively static dielectric constant measurements were made on a heterodyne beat apparatus.[9] Refractive indices were taken with a Pulfrich refractometer, densities with a chainomatic Westphal balance (Table I), and viscosities with Cannon–Fenske–Ostwald type viscometers.[10]

Table II gives the dielectric constants ϵ' and losses, ϵ'', at the wave lengths λ_0 = 1.25, 3.22 and 10.0 cm. as well as the so-called static dielectric constants, ϵ_0, measured at 577 meters and the optical dielectric constant, ϵ_∞, obtained as described below. The accuracy of the ϵ_0 measurements was better than 1%, while the precision on the microwave

Table II

Dielectric Data

t, °C.	ϵ_∞ (calcd.)	ϵ_∞ (arc)	ϵ_0	λ_0	ϵ'	ϵ''
			Ethyl acetate			
3				1	4.91	1.60
	2.03	2.48	6.40	10	6.41	0.42
20				1	4.95	1.51
	2.00	2.48	6.04	3	5.81	0.92
				10	6.06	0.33
40				1	4.88	1.31
	1.97	2.48	5.63	3	5.53	0.69
				10	5.71	.24
60	1.94	2.48	5.22	3	5.21	.53
			Isoamyl acetate			
20				1	3.35	1.04
	2.09	2.31	4.72	3	4.10	0.87
				10	4.61	.42
50				1	3.41	.88
	2.05	2.31	4.34	3	4.82	.64
				10	4.33	.27
			Cetyl acetate			
35				1	2.56	.27
	2.14	2.24	3.19	3	2.76	.27
				10	2.97	.22
55				1	2.56	.27
	2.12	2.23	3.09	3	2.76	.25
				10	2.94	.20
75				1	2.56	.27
	2.09	2.25	2.99	3	2.75	.22
				10	2.89	.15
			Octadecyl acetate			
35				1	2.51	.25
	2.15	2.23	3.07	3	2.68	.22
				10	2.92	.21
55	2.13	2.23	2.98	1	2.52	.25
				10	2.85	.17
75	2.10	2.23	2.89	1	2.52	.25
				10	2.80	.14
			Decyl stearate			
40				1	2.29	.135
	2.13	2.16	2.81	3	2.40	.168
				10	2.58	.181
60				1	2.29	.140
	2.11	2.15	2.73	3	2.41	.178
				10	2.58	.164
80	2.09	2.15	2.65	1	2.26	.140
				10	2.56	.143
			Tetradecyl palmitate			
50				1	2.30	.156
		2.17	2.66	10	2.52	.176
82	2.10	2.17	2.72	1	2.28	.16
				10	2.54	.152
			Tetradecyl stearate			
50		2.15	2.67	1	2.28	.126
82		2.16	2.57	1	2.28	.145
			Cetyl stearate			
60				1	2.28	.126
	2.12	2.13	2.61	3	2.35	.141
				10	2.46	.130
80				1	2.26	.140
	2.10	2.13	2.54	3	2.36	.138
				10	2.47	.118
			Tristearin			
80				1	2.31	.089
	2.15	2.18	2.74	3	2.39	.124
				10	2.49	.124
90	2.13	2.18	2.735	1	2.31	.088
				3	2.39	.122
				10	2.49	.124
			Distearin			
80				1	2.48	.204
	2.14	2.30	3.25	3	2.65	.272
				10	2.88	.305
90				1	2.49	.226
	2.12	2.26	3.22	3	2.67	.282
				10	2.92	.272
			Monostearin			
80				1	2.87	.45
	2.14	2.58	4.84	3	3.13	.64
				10	3.75	.81
90				1	2.87	.48
	2.12	2.53	4.74	3	3.22	.68
				10	3.87	.73
			Ethylene dimyristate			
70				1	2.44	.26
	2.14	2.19	2.98	3	2.64	.28
				10	2.87	.23
80	2.12		2.98	3	2.66	.20
				10	2.87	.22
			Ethylene dipalmitate			
75				1	2.41	.21
	2.14	2.23	2.89	3	2.58	.22
				10	2.77	.20
			Ethylene distearate			
80				1	2.39	.15
	2.14	2.26	2.79	3	2.53	.19
				10	2.69	.18

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(5) W. M. Heston, Jr., E. J. Hennelly and C. P. Smyth, *ibid.*, **70**, 4093 (1948).

(6) H. L. Laquer and C. P. Smyth, *ibid.*, **70**, 4097 (1948).

(7) W. M. Heston, Jr., A. D. Franklin, E. J. Hennelly and C. P. Smyth, *ibid.*, **72**, 3443 (1950).

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(9) G. L. Lewis and C. P. Smyth, *J. Chem. Phys.*, **7**, 1085 (1939).

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measurements was 0.5% for ϵ' and 3% for ϵ''. The molar refractions were calculated from the refractive indices, an appropriate amount was added for atomic polarization, and the ϵ_∞ values were calculated from the resultant sum of the electronic and atomic polarizations, $P_E + P_A = M(\epsilon_\infty - 1)/d(\epsilon_\infty + 2)$.

The amount to be added for atomic polarization was calculated on the basis of the induced polarization, $P_E + P_A$ = 24.5 cc., found for ethyl acetate.[11] This value is 2.6 cc. greater than the molar refraction for the sodium D line. Therefore, to the molar refraction of all the esters was added 2.6 cc. plus 0.1 cc. for every CH_2 group in excess of the number contained in ethyl acetate.[12] Miles[13] found the atomic polarization of ethyl alcohol to be zero and, accordingly, no correction was made for the hydroxyl groups in monostearin and distearin. The ϵ_∞ values calculated in this manner and designated ϵ_∞(calcd.) in Table II do not agree with those obtained from the arc plots and designated ϵ_∞ (arc).

Discussion of Results

In previous papers[7,12] of the series, the dielectric losses, ϵ'', have been plotted against the dielectric constants, ϵ', by the method of Cole and Cole[14] and used to obtain the critical wave lengths, λ_m, at which the loss is a maximum, and the empirical parameter, α, which describes the breadth of distribution of the relaxation times. When this generally satisfactory procedure was employed in the present work, it was found that, for some substances, the value of ϵ_∞ calculated in the usual way lay so far from the arc through the other points that it seemed best to disregard it in drawing the curve and obtain a value ϵ_∞(arc) from the curve for comparison with the value of ϵ_∞(calcd.). Table III gives the values of λ_m and α together with the corresponding viscosities η.

TABLE III

VALUES OF VISCOSITY (CENTIPOISES), CRITICAL WAVE LENGTH (CM.) AND DISTRIBUTION PARAMETER

	t, °C.	η	λ_m	α
Ethyl acetate	3	...	0.90	0.09
	20	0.457	.82	.06
	40	.372	.68	.04
	60	.331	.58	..
Isoamyl acetate	20	.805	1.6	.10
	50	.590	1.2	.08
Cetyl acetate	35	4.79	2.5	.29
	55	3.10	2.1	.26
	75	2.09	1.7	.24
Octadecyl acetate	35	6.39	2.8	.29
	55	4.05	2.2	.24
	75	2.76	1.8	.19
Decyl stearate	40	10.9	5.8	.34
	60	6.94	4.5	.26
	80	4.21	3.5	.14
Tetradecyl palmitate	50	....	4.5	.24
	70	....	3.6	.19
Cetyl stearate	60	9.87	3.8	.28
	80	6.23	2.7	.13
Monostearin	80	27.3	8.3	.22
	90	18.3	6.9	.24
Distearin	80	15.1	6.6	.31
	90	11.4	4.7	.30
Tristearin	80	14.6	7.8	.47
	90	11.1	7.8	.47
Ethylene dimyristate	70	5.95	2.5	.21
	80	5.16	..	..
Ethylene dipalmitate	75	6.40	3.0	.22
Ethylene distearate	80	8.04	3.4	.22

The data, as indicated in Figs. 1 and 2, conform well to arc plots if the calculated values for ϵ_∞ are disregarded. For ethyl acetate the difference between the calculated ϵ_∞ and the intercept of the arc with the ϵ' axis amounts to 0.48 at 20°. The large differences are well beyond the experimental errors and suggest that the acetates may possess another dispersion region beyond the microwave region resulting from the libration of a molecular segment.

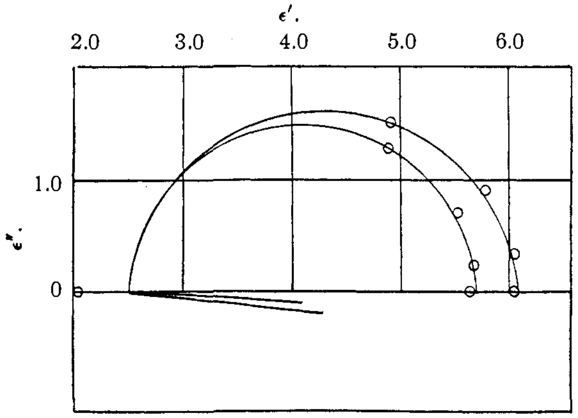

Fig. 1.—Arc plots for ethyl acetate (upper curve, 20°; lower curve, 40°).

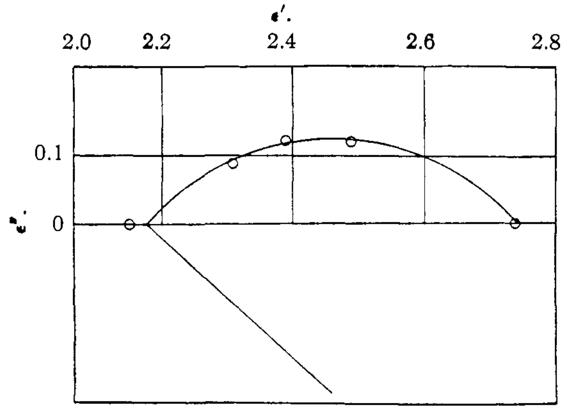

Fig. 2.—Arc plot for tristearin at 80°.

Measurements made at 20° on ethyl acetate in heptane show a critical wave length of 0.42 cm., while that of pure ethyl acetate, being 0.82 cm., is almost twice as great. The viscosity of heptane, 0.416 centipoise, is close to the value 0.457 centipoise found for pure ethyl acetate. The longer critical wave length in the pure ethyl acetate is presumably due to dipole–dipole interaction. The distribution of relaxation times is greater in the solution than in the pure liquid, α for the solution being 0.16 at 20°, while that for the pure liquid is 0.06. For small molecules, a value of α higher in solution than in the pure state is not exceptional. The same behavior has been observed, for example, with t-butyl chloride in the pure state and in a variety of solvents.[12]

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[11] C. T. Zahn, *Physik. Z.*, **33**, 730 (1932).

[12] E. J. Hennelly, W. M. Heston, Jr., and C. P. Smyth, THIS JOURNAL, **70**, 4102 (1948).

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[14] R. H. Cole and R. S. Cole, *J. Chem. Phys.*, **9**, 341 (1941).

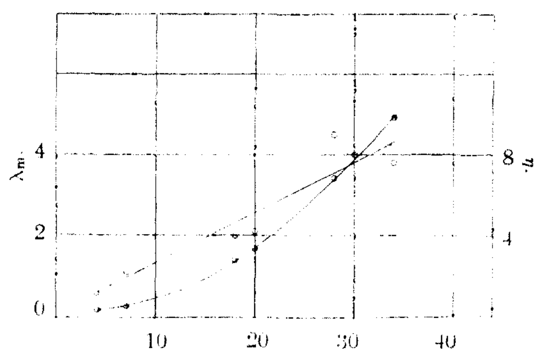

Fig. 3.—Dependence of critical wave lengths and viscosities of esters at 60° upon chain length (hollow circles, critical wave lengths; half-filled circles, viscosities).

In Fig. 3, the values of the critical wave lengths and the viscosities of the monocarboxylic acid esters measured at or interpolated to 60° are plotted against the number of carbon atoms in the molecule. The critical wave lengths for the acetates seem to flatten off somewhat with increasing molecular length in such a way as to suggest an increase in segment orientation. On the other hand, the higher values for the three much longer molecules seem to decrease with increasing chain length, but this is probably not significant because of the larger probable errors for these substances. If all of these points are represented by a single straight line, the deviations from this line are somewhat larger than the probable experimental errors. However, the critical wave length and viscosity curves are very similar to the corresponding curves[12] for the alkyl bromides at 55°. The viscosities of the esters are slightly lower than those of alkyl bromides of approximately the same molecular length and the critical wave lengths are only about half as large. The points give no evidence of increase or decrease resulting from moving the molecular dipole from a location near the end of the molecule to one near the middle, although a small effect may well be obscured by the experimental errors. In both locations segment orientation by twisting around the C–C bonds, presumably, contributes largely to the orientation polarization. The correlation of the critical wave lengths with viscosity is shown in Fig. 4 for both the bromides and the esters. In the bromides, the orienting C–Br dipole is at the extreme end of the molecular chain, while, in the ethyl esters, the polar COOC-group is separated from the end by a methyl group and, in the three longer ester molecules, it is remote from the end. Possibly, the frictional forces on the bromine atom are responsible for the slightly higher viscosities and the much higher critical wave lengths of the alkyl bromides.

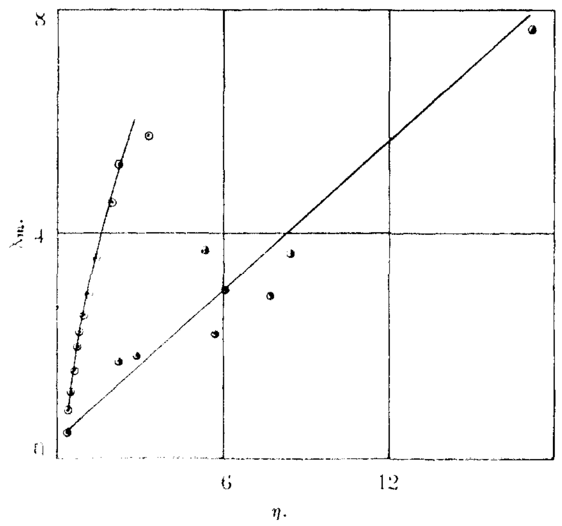

Fig. 4.—Correlation of the critical wave lengths with viscosity for alkyl bromides (hollow circles) at 55° and esters (half-filled circles) at 75°.

The distribution parameter, α, which has been shown previously to increase with increasing chain length and viscosity[12,15] tends to increase as the size of the ester molecule increases and decrease with increasing temperature. The latter effect indicates that the manner of orientation is becoming more uniform. It may be that the expansion of the liquid has reduced the effect of the arrangement of the neighboring molecules in the orientation process. For one particular orienting segment, there may be many relaxation times possible because of the manner in which the molecules surrounding the orienting molecule are located. On the other hand, for a particular arrangement of the surrounding molecules, the molecule in question may choose to orient in one of several possible ways depending on how the internal energy is distributed. In all probability, both of these effects are significant in determining the breadth of the distribution.

The thermodynamic quantities for the activated state have been calculated for the processes of viscous flow and dielectric relaxation by the methods previously employed.[12,16] As was found for the bromides,[12] the dependence of the free energies of activation for the two processes upon molecular length is similar, the ratio of the activation energy for dielectric relaxation to that for viscous flow being about 0.6. This difference has been attributed to the fact that viscous flow involves both translational and rotational motion, while dielectric relaxation involves only rotational.[12,15,17] Except for monostearin and distearin, all the enthalpies of activation are smaller than the corresponding free energies of activation, and, consequently, the entropies of activation are negative. The latter become more negative as the molecular complexity increases. A negative entropy of activation indicates that there are fewer configurations possible in the activated state and suggests a certain degree of coöperation in the orientation process.

For the stearates, the ethylene diesters and tristearin, the differences between the calculated and graphical values of ϵ_∞ are small and within the experimental error, which is relatively large because of the small differences between ϵ_0 and ϵ_∞ for these compounds. Monostearin and distearin should show the behavior both of esters and of alcohols due to the presence of both the carboxy and the hy-

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(16) S. Glasstone, K. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941, Chap. IX.

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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 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

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

[CONTRIBUTION NO. 1661 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

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

BY ROGER NEWMAN AND RICHARD M. BADGER

RECEIVED FEBRUARY 25, 1952

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)

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[1] This research was supported by the Office of Naval Research under Contract N6-ori-102, VI.

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[4] E. J. Ambrose, A. Elliott and R. B. Temple, *Proc. Roy. Soc.* (*London*), **206A**, 192 (1951).