

toluene. The aqueous layer was acidified with hydrochloric acid and the product extracted with toluene. The toluene layer was washed with water; the toluene was evaporated and the product distilled, b.p. 222–230°/1 mm., 180 g., (49.5%),  $n_D^{20}$  1.6188.

*Anal.* Calcd. for  $C_{18}H_{14}O_2$  (278.3): C, 77.7; H, 5.1. Found: C, 77.4; H, 5.1.

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compounds, C. A. Reilly for NMR spectra, F. S. Mortimer for aid in the evaluation of the infrared absorption spectra, E. R. Barnum for helpful discussions, and the Materials Laboratory, Wright Air Development Center for permission to publish this information.

EMERYVILLE, CALIF.

[CONTRIBUTION FROM THE RESEARCH LABORATORY, PUREX CORPORATION, LTD.]

## *N*-Halogen Compounds. II.<sup>1,2</sup> The N—Cl Stretching Band in Some *N*-Chloroamides. The Structure of Trichloroisocyanuric Acid

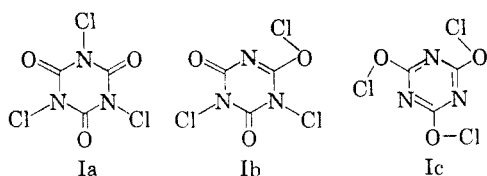
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The infrared spectrum of solid trichloroisocyanuric acid is interpreted as confirming the keto structure Ia of Chattaway and Wadmore. The 650–900  $\text{cm}^{-1}$  region of thirteen *N*-chloroamides and of some of their congeners was examined. All the chlorinated cyanuric acids and benzenesulfonamide derivatives studied as well as 1,3-dichloro-5,5-dimethylhydantoin contained a band between 762 and 803  $\text{cm}^{-1}$  which is probably essentially an N-Cl stretching frequency. Compounds containing N-Cl attached to more weakly electronegative groups, such as *N*-chlorosuccinimide and *N*-chloroacetamide, did not have such a band. The preparation of some halogen derivatives of cyanuric acid is described.

As part of a program of examining solid compounds for bleaching activity we have run the infrared spectra of a number of *N*-chloroamides. The main object has been to build a library of reference spectra for identification purposes, but we have studied some of them in detail when structural questions arose, and have sought new spectra-structure correlations.

Early in the work it became of practical importance to know whether crystalline trichloroisocyanuric acid (I) was, as Chattaway and Wadmore<sup>4</sup> believed, all in the keto form Ia, or whether it was in some tautomeric form such as Ib or Ic, or was a mixture of two or more such forms.



The available chemical evidence,<sup>1,4</sup> which we confirmed by a molecular weight determination, make it quite certain that I is a trimer,  $(CClNO)_3$ . Estimates of bond and resonance energies definitely

(1) Paper I, R. C. Petterson and U. Grzeskowiak, *J. Org. Chem.*, **24**, 1414 (1959).

(2) Presented before the Division of Organic Chemistry of the American Chemical Society, Atlantic City, N. J., September 16, 1959.

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(4) F. C. Chattaway and J. M. Wadmore, *J. Chem. Soc.*, **81**, 191 (1902).

indicate that Ia should be the most stable form, thermodynamically. Nevertheless, in the absence of physical evidence for the location of the chlorine atoms, no definite conclusion could be reached.

No physical evidence for the location of the chlorine in any chloroamide has been found in the literature. However, the infrared spectra of six bromoamides reported by Lacher, Olson, and Park<sup>5</sup> were in accord with a keto-*N*-bromo structure, and a number of amides not containing positive halogen, including cyanuric acid, have been shown<sup>6,7</sup> to be completely in the keto form in the solid state by both x-ray and infrared studies.

The infrared spectrum of crystalline trichloroisocyanuric acid (Fig. 1 and Table I) turned out to be surprisingly simple, as it exhibited only six well-defined bands. In a twelve-atom molecule, this scarcity of bands indicates a symmetrical and probably a planar structure, and favors structure Ia or Ic over forms such as Ib. The strong band near 1740  $\text{cm}^{-1}$  must be due to carbonyl absorption and the shift in its frequency from 1710  $\text{cm}^{-1}$  in cyanuric acid<sup>6</sup> is in the direction expected. The frequency in cyanuric acid may be lowered by hydrogen bonding which is not possible for I, and it seems reasonable for an average of one chlorine substituent *alpha* to the carbonyl, and probably in the same plane, to raise the C=O stretching frequency

(5) J. R. Lacher, G. G. Olson, and J. D. Park, *J. Am. Chem. Soc.*, **74**, 5578 (1952).

(6) R. Newman and R. M. Badger, *J. Am. Chem. Soc.*, **74**, 3545 (1952).

(7) S. Mizushima, T. Simanouti, S. Nagakura, K. Kuratani, M. Tsuboi, H. Baba, and O. Fujioka, *J. Am. Chem. Soc.*, **72**, 3490 (1950).

TABLE I  
 FREQUENCIES (CM.<sup>-1</sup>) OBSERVED FOR TRICHLOROISOCYANURIC ACID

Film, evaporated on AgCl	1739	1360	1335	1154	800	696
Mull, in Nujol	1742	—	—	1153	800	698
Assignment	C=O		Ring stretching		N—Cl	?

 TABLE II  
 FREQUENCIES IN THE 650-900 CM.<sup>-1</sup> REGION

Compound	Location of Bands						N-Cl Stretching	
Cyanuric Acid Derivatives (See Figs. 2 and 3)								
Dichloroisocyanuric acid	790	748	709	699			790	
Sodium dichloroisocyanurate	890	803	789	755	749	742	803,789	
Sodium dichloroisocyanurate dihydrate	789	749	738	728	706		789	
Potassium dichloroisocyanurate	787	764	746	740	699		787	
Potassium dibromoisocyanurate	754	734					—	
Benzenesulfonamide Derivatives (See Figs. 4 and 5)								
<i>p</i> -(Dichlorosulfamyl)benzoic acid	865	845	822	782	763	755	683	782 (755?)
<i>p</i> -Sulfamylbenzoic acid	864	767	687					—
<i>N,N</i> -Dichlorobenzenesulfonamide	891	851	771	749	683			771
Benzenesulfonamide	904	840	755	688				—
<i>N,N</i> -Dichloro- <i>p</i> -toluenesulfonamide	892	814	800	762	698			762 (800)
<i>p</i> -Toluenesulfonamide	809	704	667					—
<i>N,N,N',N'</i> -Tetrachlorotoluene-2,4-disulfonamide	889	849	842 sh.		774	744	[711]	774 (744?)
Toluene-2,4-disulfonamide	896	835	700	672				—
Hydantoin Derivatives (See Fig. 6)								
1,3-Dichloro-5,5-dimethylhydantoin	784	732	712					784?
1-Chloro-5,5-dimethylhydantoin	795	760	744	663				?
5,5-Dimethylhydantoin	801	769						—
1,3-Dibromo-5,5-dimethylhydantoin	855	770	734					—
Others								
<i>N</i> -Chlorosuccinimide	818	650 sh.						?
Succinimide	850	821 (733)						—
<i>N</i> -Bromosuccinimide	814	650 sh.						—
<i>N</i> -Iodosuccinimide	818							—
<i>N</i> -Chloroacetamide	826							?
Acetamide	876							—

by 25-30 cm.<sup>-1</sup> The strong doublet at 1335 and 1360 cm.<sup>-1</sup> and the weak band at 1154 cm.<sup>-1</sup> resemble fairly closely the main ring-stretching bands<sup>6</sup> of cyanuric acid, which has a strong band at 1470 cm.<sup>-1</sup> and a weak doublet at 1050 and 1065 cm.<sup>-1</sup>. *s*-Triazine differs greatly, having ring stretching frequencies at 1556, 1410, and 675 cm.<sup>-1</sup><sup>9</sup> Thus it seems almost certain that trichloroisocyanuric acid has structure Ia in the solid state.

The two remaining strong bands at 698 and 800 cm.<sup>-1</sup> are more difficult to explain. The former is, perhaps fortuitously, similar to an unidentified band at 695 cm.<sup>-1</sup> in cyanuric acid and no assignment can be made for it at present. The 800 cm.<sup>-1</sup> band is probably not related to the weak 807 cm.<sup>-1</sup> frequency of cyanuric acid which has been tenta-

tively ascribed<sup>6</sup> to N-H bending; it might possibly be due to N-Cl stretching. The few known N-Cl bands have rather lower frequencies, *viz.* NH<sub>2</sub>Cl, 686; NHCl<sub>2</sub>, 687 and 666; and NCl<sub>3</sub>, 652 cm.<sup>-1</sup>,<sup>10,11</sup> but certain substituents on the nitrogen should cause an increase in an N-Cl stretching frequency. There is no obvious reason why N-Cl stretching should not vary at least as much as C-Cl stretching, which is found from 600 to 800 cm.<sup>-1</sup><sup>12</sup>

In the hope of verifying this tentative assignment the spectra of thirteen N-Cl compounds of several types and of some of their N-H and N-Br congeners were run as mulls and the curves examined for evidence of bands due to N-Cl. The frequencies of

(10) G. E. Moore and R. M. Badger, *J. Am. Chem. Soc.*, **74**, 6076 (1952).

(11) A. G. Pulford and A. Walsh, *Trans. Far. Soc.*, **47**, 347 (1951), state that a 595 cm.<sup>-1</sup> band in nitrosyl chloride corresponds essentially to N-Cl stretching.

(12) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley & Sons, New York, N. Y., 2nd ed., 1958, p. 330.

(8) According to E. J. Corey and H. J. Burke, *J. Am. Chem. Soc.*, **77**, 5418 (1955), equatorial *alpha* substitution of chlorine in cyclohexanones raises the carbonyl frequency by 26-31 cm.<sup>-1</sup>

(9) J. E. Lancaster and N. B. Colthup, *J. Chem. Phys.*, **22**, 1149 (1954).

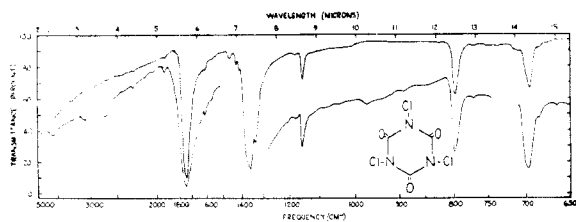


Fig. 1. Infrared spectrum of trichloroisocyanuric acid in Nujol mull (lower) and as a crystalline film (upper)

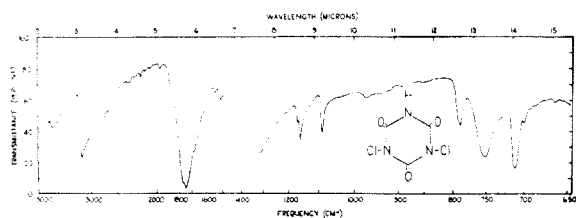


Fig. 2. Infrared spectrum of dichloroisocyanuric acid (Nujol)

bands found in the 650–900  $\text{cm}^{-1}$  are listed in Table II. Bands near 720  $\text{cm}^{-1}$  are unfortunately distorted or obscured by the Nujol peak in this region but no practical way of avoiding the use of the oil was found (see Experimental).

The spectra of six cyanuric acid derivatives are presented in Figs. 1–3. The N-Cl compounds all have a medium intensity band near 800  $\text{cm}^{-1}$ , which is at 800  $\text{cm}^{-1}$  in trichloroisocyanuric acid, shifts to 787–790  $\text{cm}^{-1}$  in dichloroisocyanuric acid (II) and its sodium and potassium salts, but is absent in potassium dibromoisocyanurate. In the anhydrous sodium salt this band has split into a 789, 803  $\text{cm}^{-1}$  doublet, rather weaker than the single band in the dihydrate. In Figs. 1 and 2 I, with three N-Cl bonds, has a stronger peak, relative to the carbonyl stretching band, than II, which has only two N-Cl bonds. It seems likely that the N-Cl stretching frequencies for these chlorinated cyanuric acid derivatives lie between 785 and 803  $\text{cm}^{-1}$ .

Comparison of the spectra of four aromatic sulfonamides with those of their *N*-chloro derivatives (Figs. 4 and 5) reveals that all the bands present in the 650–900  $\text{cm}^{-1}$  region of each sulfonamide seem to be present (slightly shifted) in the corresponding N-Cl compound. In addition, each chloro compound has a band between 762 and 782  $\text{cm}^{-1}$ , probably an N-Cl stretching frequency; three of them also exhibit another band in the 744–800  $\text{cm}^{-1}$  region, which may be a second N-Cl band, namely *p*-(dichlorosulfamyl)benzoic acid (755  $\text{cm}^{-1}$ , Fig. 4), *N,N,N',N'*-tetrachlorotoluene-2,4-disulfonamide (744  $\text{cm}^{-1}$ , Fig. 5), and *N,N*-dichloro-*p*-toluenesulfonamide (800  $\text{cm}^{-1}$ , Fig. 5).

In the hydantoin (Fig. 6) the two possessing N-H groups have weak bands at 795–801  $\text{cm}^{-1}$  which seem to be absent in the dichloro and dibromo compounds and may be caused by N-H. The medium intensity peak at 784  $\text{cm}^{-1}$  in 1,3-dichloro-5,5-dimethylhydantoin may be an N-Cl

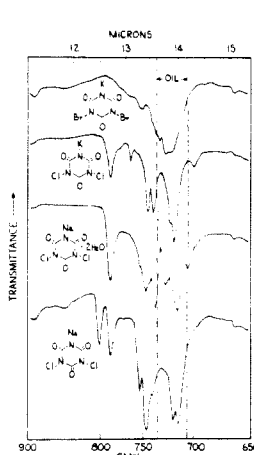


Fig. 3

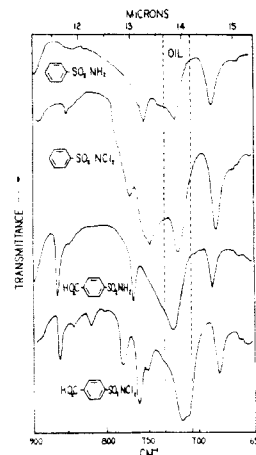


Fig. 4

Fig. 3. Infrared spectra of sodium dichloroisocyanurate and its dihydrate, potassium dichloroisocyanurate, and potassium dibromoisocyanurate (Nujol)

Fig. 4. Infrared spectra of *p*-(dichlorosulfamyl)benzoic acid, *p*-sulfamylbenzoic acid, *N,N*-dichlorobenzenesulfonamide, and benzenesulfonamide (Nujol)

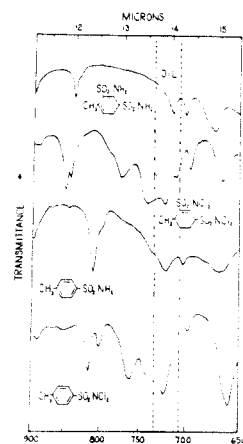


Fig. 5

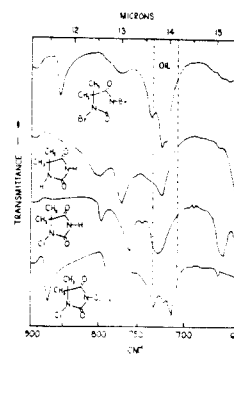


Fig. 6

Fig. 5. Infrared spectra of *N,N*-dichloro-*p*-toluenesulfonamide, *p*-toluenesulfonamide, *N,N,N',N'*-tetrachlorotoluene-2,4-disulfonamide, and toluene-2,4-disulfonamide (Nujol)

Fig. 6. Infrared spectra of 1,3-dichloro-5,5-dimethylhydantoin, 1-chloro-5,5-dimethylhydantoin, 5,5-dimethylhydantoin, and 1,3-dibromo-5,5-dimethylhydantoin (Nujol)

stretching frequency, although it may be related instead to the unidentified 760–770  $\text{cm}^{-1}$  band present in the other three hydantoin. The spectrum of the 1-chloro derivative in this region seems to resemble that of the unhalogenated compound closely; no N-Cl assignment can be made.

In *N*-chlorosuccinimide no band attributable to N-Cl was found in the 650–900  $\text{cm}^{-1}$  region. It has a strong peak at 818  $\text{cm}^{-1}$  which is also present in the N-H, N-Br, and N-I derivatives (see Table II) and nothing else down to about 650  $\text{cm}^{-1}$ . *N*-chloroacetamide does not show any bands in this region either except for a broad, weak absorption near 826  $\text{cm}^{-1}$ .

From the rather large range of the frequencies which have been assigned to N-Cl stretching, it is obvious that the vibrations responsible are by no means localized completely in the N-Cl group. Motions of the other groups attached to nitrogen must be involved and the mass of such substituents ought to be an important factor. In the case of the chlorosulfonamides, other influences must be canceling out the effect of the large mass of the sulfur atom relative to carbon for the frequencies for N-Cl in the chlorosulfonamides to come out in the same range as some of those in chloroamides.

Electronic effects must be quite important, as it is striking that only those compounds with rather strongly electronegative substituents on the N-Cl group show N-Cl bands in the region studied. For instance, although both trichlorocyanuric acid and *N*-chlorosuccinimide contain the —CONClCO— group, the fact that this group is bound to a highly electronegative —NCICONCl— grouping in the former but to the electropositive —CH<sub>2</sub>—CH<sub>2</sub>— group in the latter evidently results in a great difference in N-Cl frequency in the expected direction. On the other hand, it is surprising that the salts of dichloroisocyanuric acid have bands at only slightly lower frequencies than that of the parent acid.

Not much diagnostic use can be made of these empirical correlations at present. Fortunately, the presence of an N-Cl group in an amide can generally be readily detected iodometrically if it is assumed that the chlorine in chloroamides is always bound to nitrogen, a view which the foregoing evidence tends to support.

#### EXPERIMENTAL<sup>13</sup>

**Infrared spectra.** The infrared spectra described were run as mulls in Nujol between sodium chloride discs except for the crystalline film curve of I (Fig. 1). The latter is the spectrum of ten thin layers of crystals on a silver chloride disc deposited by rapid evaporation of successive drops of a fresh dilute solution of I in acetonitrile; a silver chloride disc was in the reference beam. No inert solvent capable of dissolving all the compounds of interest is known, and dispersions of N-Cl compounds in potassium bromide and potassium chloride pressed discs invariably gave spectra differing considerably from mull spectra. Decomposition was occurring in some cases, as the pellets sometimes developed orange (potassium bromide) or green (potassium chloride) colors. Deposition of crystalline films from solution without decomposition was not always possible, and, with dichloroisocyanuric acid, the spectra of films on silver chloride differed both from films on sodium chloride and (Bios Laboratories). We thank the companies mentioned for gifts of: *N,N,N',N'*-tetrachlorotoluene-2,4-disulfonamide from that of mulls. With the trichloro compound I, the curve from a film on silver chloride was identical with that

(13) Melting points are uncorrected. The infrared spectra were run on a Perkin-Elmer Model 21 Spectrometer having a sodium chloride prism by Mr. Everett P. Honorof. It was frequently calibrated against ammonia. Some preliminary spectra were run at the University of Southern California by Mr. William J. Schenck, to whom we are indebted for helpful advice on techniques.

from a mull but different from that of a film on sodium chloride. Mull spectra were always reproducible.

**Materials.** Pure trichloroisocyanuric acid was obtained by recrystallization of commercial material from warm ethylene chloride in the form of colorless needles, m.p. 246–247° dec., (lit.<sup>4</sup> m.p. about 245°).

**Anal.** Calcd. for C<sub>3</sub>N<sub>3</sub>O<sub>3</sub>Cl<sub>3</sub>: mol. wt., 232; Av. Cl, 91.53. Found: mol. wt. (cryoscopic, in benzene<sup>14</sup>), 237; Av. Cl, 91.13.

Dichloroisocyanuric acid separated when an ice-cooled aqueous solution of its sodium salt was acidified with cold 3% sulfuric acid. It was collected, washed, and dried at 105° for 1.5 hr.; m.p. 226.4–226.7°. The absence of cyanuric acid as an impurity was shown by the complete solubility of the sample in acetonitrile.

**Anal.** Calcd. for C<sub>3</sub>HCl<sub>2</sub>N<sub>3</sub>O<sub>3</sub>: Av. Cl, 71.65. Found: Av. Cl, 71.58.

Crude sodium dichloroisocyanurate, kindly furnished by Westvaco Mineral Products Division, Food Machinery and Chemical Corp., crystallized from water as colorless needles which proved to be the dihydrate.

**Anal.** Calcd. for C<sub>3</sub>Cl<sub>2</sub>N<sub>3</sub>NaO<sub>3</sub>·2H<sub>2</sub>O: Av. Cl, 55.41; water, 14.05. Found: Av. Cl, 55.42; weight loss in 45 min. at 105°, 13.95.

The solid remaining after heating was sodium dichloroisocyanurate.

**Anal.** Calcd. for C<sub>3</sub>Cl<sub>2</sub>N<sub>3</sub>O<sub>3</sub>Na: Av. Cl, 64.48. Found: Av. Cl, 64.37.

Potassium dichloroisocyanurate was prepared by dissolving potassium sulfate (4.36 g.) in an iced solution of sodium dichloroisocyanurate (11.0 g.) in water (60 ml.). The colorless crystals which separated were washed with water and dried at 115°.

**Anal.** Calcd. for C<sub>3</sub>Cl<sub>2</sub>N<sub>3</sub>O<sub>3</sub>K: Av. Cl, 60.08. Found: Av. Cl, 59.06.

To a solution of potassium bromide (23.8 g., 0.2 mole) in water (500 ml.) was added a solution of sodium dichloroisocyanurate (22 g., 0.1 mole) in water (200 ml.); crude potassium dibromoisocyanurate (26 g., 79% yield) was obtained by filtering, washing, and drying at 115° the colorless crystals which separated. Aqueous solutions of the substance liberated bromine on treatment with concd. hydrochloric acid. Recrystallization from water was accompanied by decomposition.

**Anal.** Calcd. for C<sub>3</sub>Br<sub>2</sub>KN<sub>3</sub>O<sub>3</sub>: Av. Br, 98.36. Found: Av. Br, 93.74.

*p*-Toluene-2,4-disulfonamide, obtained by reduction of its tetrachloro derivative with excess concd. aqueous ammonia, was recrystallized from water three times, m.p. 185–186° (with previous sintering near 174°) (lit.<sup>15</sup> m.p. 186–187°).

The samples of 5,5-dimethylhydantoin and its 1-chloro and 1,3-dichloro derivatives used have been described previously.<sup>1</sup> *N*-chloroacetamide, made by a known method,<sup>16</sup> melted at 110° (lit.<sup>16</sup> m.p. 110°).

The following compounds were dried *in vacuo* over phosphorus pentoxide, and used without further purification: benzene- and *p*-toluenesulfonamide, and *N*-bromosuccinimide (Eastman Kodak Co.); *N*-iodosuccinimide (Arapahoe Chemicals, Inc.); and *p*-(dichlorosulfamyl)benzoic acid (Dow Chemical Co.); 1,3-dibromo-5,5-dimethylhydantoin (Glyco Products Co., Inc.); *N,N*-dichlorobenzenesulfonamide and *N,N*-dichloro-*p*-toluenesulfonamide (Monsanto Chemical Co.); and *p*-sulfamylbenzoic acid (Boots Pure Drug Co., Ltd., England).

**Acknowledgments.** The authors are grateful to Dr. Robert C. Ferris for encouragement, and to the Purex Corporation, Ltd. for permission to publish.

SOUTH GATE, CALIF.

(14) Determined by Mr. Laszlo L. Low.

(15) C. Fahlberg, *Ber.*, 12, 1048 (1879).

(16) A. Hantzsch and F. E. Dollfus, *Ber.*, 35, 252 (1902).