Studies on the Molecular Structures of Some Cyanuric Compounds by Electron Diffraction

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Recently, heterocyclic compounds have been studied theoretically from various points of view. We cannot admit, however, that we have so many experimental data available for this theory as for other spheres of study. In order to obtain such data, it may be necessary that more electron diffraction investigations be made on such heterocyclic compounds.

In this paper two kinds of cyanuric compounds, that is, cyanuric chloride and melamine are taken up. These compounds have a good symmetry, which makes it possible to measure the whole scheme of the molecules by comparatively few parameters. Therefore these compounds may be considered to be quite suitable for electron diffraction investigations.

Several crystalline cyanuric compounds have been investigated by the X-ray diffraction method[1–5]. We will mention here only the value given in Hughes' report of 1941 on melamine as it is directly related to this paper, which suggests that[1], $C\text{-}N_{ring}=1.33$–1.35 Å, $C\text{-}N_{outer}=1.35$–1.36 Å and $\angle N_r\text{-}C\text{-}N_r=123$–$125°$ within the error limit of about 0.02 Å. Reports concerning other cyanuric compounds will be quoted hereafter, when necessary.

Experimental

Each sample, cyanuric chloride (bp. 190°C) and melamine (sublimed over 300°C), was recrystallized before use. The electron diffraction photographs were made with these crystalline samples, which were vaporized into the apparatus previously described, with the help of a high temperature nozzle, newly designed for this purpose[7,8]. Gold foils were used for calibration of the electron wave length which was approximately 0.05–0.06 Å. The positions of halos were measured visually, and listed in Table I. The characteristic features of the photographs were represented by the visual curves $I_{vis}(q)$ and shown at the top of Fig. 3 and Fig. 5. From these curves, radial distribution curves were obtained by punched card summation of the formula

$$rD(r)=\sum_q I_{vis}(q)\exp(-aq^2)\sin(\pi qr/10)$$

with a chosen to give $\exp(-aq^2)=0.20$ at $q=80$.

The theoretical intensity curves

$$I(q)=\sum_{i\neq j}\sum(Z_iZ_j/r_{ij})\exp(-b_{ij}q^2)\sin(\pi qr_{ij}/10)$$

were calculated also for various models and compared with the visual curves.

TABLE I

THE OBSERVED q-VALUES FOR CYANURIC CHLORIDE AND MELAMINE

Max.	Min.	Cyanuric chloride	Melamine
1		17.2	18.6
2		(20.1)	(20.4)
	2	22.2	23.8
3		24.0	26.2
	3	26.1	28.1
4		28.0	31.1
	4	30.2	33.1
5		32.6	35.9
	5	36.0	
6		38.9	(39.2)
	6		41.9
7		(43.0)	45.6
	7	45.2	49.8
8		47.8	53.2
	8	52.9	57.4
9		55.3	62.0
10		(59.7)	
11		64.0	
12		70.2	
13		74.9	
14		78.9	

The values in the branckets were not used for quantitative comparisons.

Interpretation

In 1935, Knaggs[5] suggested that cyanuric triazide requires two unequal $C\text{-}N_r$ distances of 1.31 and 1.38 Å, corresponding essentially

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1) E.W. Hughes, *J. Am. Chem. Soc.*, 63, 1737 (1941).

2) J.L. Hoard, ibid., 60, 1194 (1938).

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

4) E.W. Hughes. *J. Chem. Phys.*, 3, 1 (1935).

5) J.E. Knaggs, *Proc. Roy. Soc.* (London), **A150**, 576 (1935).

6) T. Yuzawa and M. Yamaha, This Bulletin, 26, 414 (1953).

7) H. Oosaka and Y. Akimoto, ibid., 26, 433 (1953).

8) L. Pauling and Sturdivant, *Proc. Nat. Acad. Sci.*, 23, 615 (1937).

to alternating double and single bonds. However, throughout all the X-ray diffraction investigation on various cyanuric compounds, this is the only work that suggested the inequality of cyanuric bonds. As the theoretical treatment of Pauling and Sturdivant[8] showed, such inequality seems very unusual, especially in the gaseous state. Moreover our result on the radial distribution curves does not support such a conclusion anyway. Therefore, in this work, we assumed the D_{3h} symmetry of the cyanuric ring: namely the equality of all cyanuric bonds. The same symmetry and co-planality were assumed throughout the whole molecular shapes[9]. Therefore, for cyanuric chloride only 3 parameters: C-N_r, C-Cl, and N_r-C-N_r. and for melamine 5 parameters: C-N_r, C-N_o, N_o-H, $\angle N_r$-C-N_r, and $\angle$H-N_o-H, are sufficient to determine the complete shapes of these molecules.

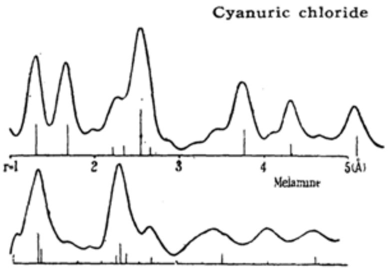

Fig. 1. Radial distribution curves for cyanuric chloride and melamine.

TABLE II
ASSUMED $<l^2_{ij}>^{1/2}$AV VALUES
($b_{ij}=(\pi^2/200)<l^2_{ij}>$AV)

Cyanuric chloride		Melamine	
C-N_r	0.044	All C-N, N-N, and C-C distances	0
C-C′	0.053		
N_r-N_r′	0.056	N_o-H	0.060
C-N_r″	0.061	All the other H-containing distances	0.083
C-Cl	0.045		
N_r-Cl′	0.057		
C-Cl″	0.072		
N_r-Cl″′	0.084		
Cl-Cl″″	0.095		

Cyanuric Chloride.—The radial distribution curve is shown at the upper part of Fig. 1. The following parameter set was the best obtained: C-N_r=1.33 Å, C-Cl=1.68 Å, and $\angle N_r$-C-N_r=125°.

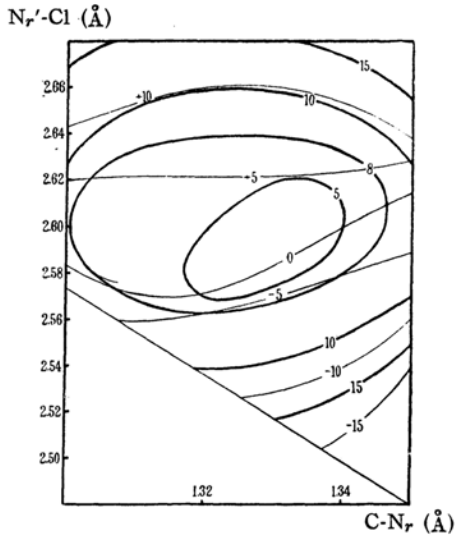

Fig. 2. Parameter chart of $q_{calc.}/q_{obs.}$ and mean deviations for cyanuric chloride.*
*Heavy lines are for $q_{calc.}/q_{obs.}$; and light curves for mean deviations. Numerical values must be multiplied by 10^{-3}.

The theoretical intensity curves were calculated for 32 models over the following parameter ranges: C-N_r=1.30–1.37 Å, C-Cl=1.60–1.70 Å, $\angle N_r$-C-N_r=115–130°, with b_{ij} values shown in Table II[10]. The q_{calc}/q_{obs} values and mean deviations of maxima and minima were calculated over all theoretical curves respectively. The relations of these values are picturized in Fig. 2 as a parameter chart which is essential for all models in the following parameter ranges: C-Cl=1.70–1.64 Å and $\angle N_r$-C-N_r=120–130°. C-N_r=1.33 Å, and N_r′-Cl=2.59 Å are the best values established from this chart. Several theoretical curves are shown in Fig. 3, and their parameters in Table III. Curve R has the best parameter set obtained from the radial distribution computation. Curves A–C were chosen to explain the differences of particular features from the visual curves. For such differences of features, a parameter chart was

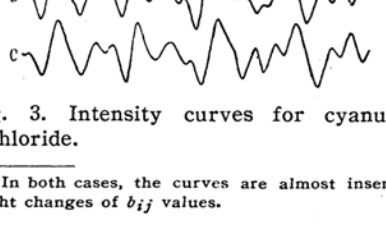

Fig. 3. Intensity curves for cyanuric chloride.

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[9] For melamine, several models, in which the planes through the N_o atom and the two H atoms are perpendicular with the ring plane, were also tested but with no sufficient changes of the curves.

[10] In both cases, the curves are almost insensitive to slight changes of b_{ij} values.

TABLE III

MODELS FOR CYANURIC CHLORIDE

Model	C-N_r (Å)	C-Cl (Å)	∠N_r-C-N_r
R	1.33	1.68	125°
A	1.32	1.70	120°
B	1.34	1.68	122.5°
C	1.34	1.66	130°

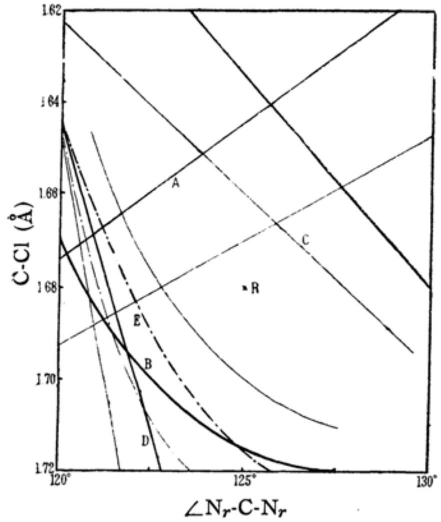

Fig. 4. Parameter chart of particular features for cyanuric chloride. Heavy lines indicate the border lines of models which have 1.34Å for C-N_r, and light lines 1.32Å for C-N_r.

Relative intensities of max. 3 and max. 4 (A), max. 5 and max.6 (B), and min. 8′ and 9′ (C), positions and shapes of max. 10 (D) and max. 13 (E) were quoted for the comparisons.

also made and shown in Fig. 4. Each line indicates where a particular feature of the intensity curves is sufficiently different from the visual curves to make them unacceptable.

Comparison of the two parameter charts leads us to the final set, C-N_r=1.33±0.02 Å, C-Cl=1.68±0.03 Å, and ∠N_r-C-N_r=125±3°. which is in complete agreement with the conclusion of the radial distribution argument.

Melamine.—The radial distribution curve is shown at the bottom of Fig. 1. The increase of the number of atoms makes the interpretation more difficult than that of the former. Overmore, the existence of hydrogen atoms makes almost all peaks considerably ambiguous. Therefore the direct determination of the 5 parameters is next to impossible. Assuming 120° for H-N_o-H and 1.04 Å for N_o-H, we can barely get to the following most possible parameter set: C-N_r= 1.34 Å, C-N_o=1.36–1.37 Å, and ∠N_r-C-N_r= 120–125°.

Twelve theoretical curves were calculated over the following ranges: C-N_r=1.32–1.38 Å, C-N_o=1.34–1.40 Å and ∠N_r-C-N_r=115–130°. N_0-H=1.04 Å and ∠H-N_o-H=120° were kept over all models. The b_{ij} values were taken as shown in Table II [10]. An effective value Z=1.25 was used for hydrogen atoms. Representative theoretical curves are shown in Fig. 5. The positions of several peaks are only sensitive for the change of the C-N_r distances. As these peaks are hardly affected by the change of the other parameters (for example, 0.02 Å changes of C-N_r distance is enough to shift Max. 5 by 1q, while 0.5 q shifts of the same peak requires the change

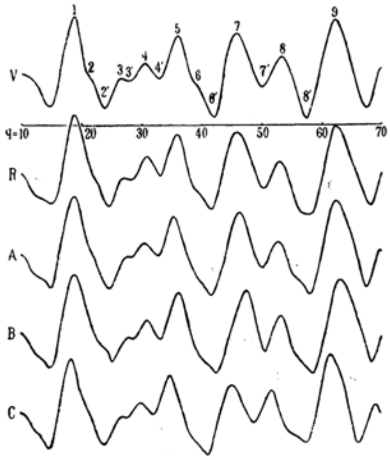

Fig. 5. Intensity curves for melamine.

TABLE IV

MODELS FOR MELAMINE

Model	C-N (Å)	C-N_o (Å)	∠N_r-C-N_r
R	1.34	1.37	123°
A	1.34	1.36	120°
B	1.32	1.34	120°
C	1.36	1.36	120°

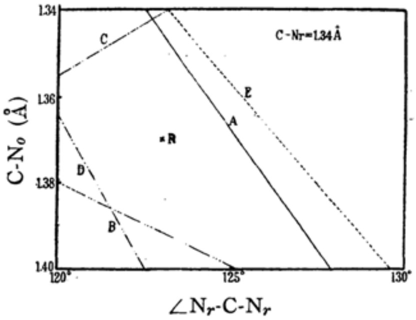

Fig. 6. Parameter chart of particular features for melamine.

Positions of max. 3 (A), max. 4 (B), max. 7 (C) and max. 8 (D), and existence of shelf between 8′ and 9 (E) were quoted for the comparisons.

of about 0.05 Å of C-N_o distance or 5° of $\angle N_r$-C-N_r), we can conclude safely that the C-N_r distance is 1.34±0.01 Å. To decide the other two parameters, the particular features are compared in Fig. 6 as a parameter chart.

Final conclusions are C-N_r=1.34±0.01 Å, C-N_o=1.37±0.03 Å and $\angle N_r$-C-N_r=123±3°.

Molecular Orbital Calculation

In order to discuss our results theoretically, simple MO calculations were applied to these compounds as well as to *sym*-trichlorobenzene and *sym*-triaminobenzene. The energy and wave function of each molecular orbital were obtained by the usual LCAO method. In the actual calculation, the exchange integral between non-adjacent atoms was neglected. Furthermore, for the Coulomb integral (α_r) and the exchange integral (β_{rs}) between two adjacent atoms, Sandorfy's values were employed, as shown in Table V[11]. Induction effect was assumed for α_r of the atoms which are next to hetero atoms to be 1/10.

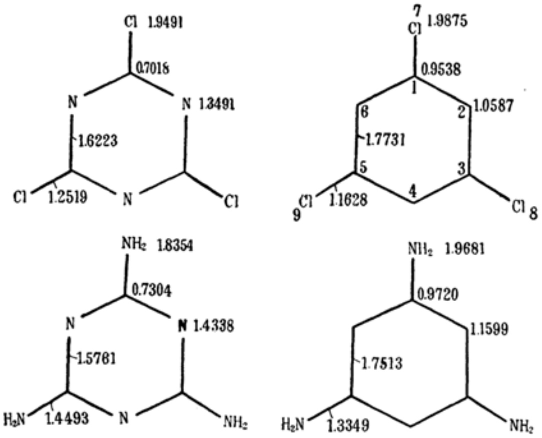

Fig. 7. Molecular diagrams by MO calculations.

By use of the molecular orbital wave function thus obtained, the electron density (q_r) and bond order (p_{rs}) were evaluated by the following equations:

$$q_r = 2\sum_n c^2_{rn}, \quad p_{rs} = 2\sum_n c_{rn}c_{sn}.$$

where C_{rn} is the coefficient of the r-th atomic wave function in the molecular orbital and the summation extends over the filled orbitals in the ground state. The results are shown in Fig 7.

TABLE V

SANDORFY'S INTEGRAL VALUES IN UNIT OF β[11]

Atom or bond	Integral value
C	4.10
N_r,N_o	5.17
Cl	5.08
C-C	1.00
C-N_r	1.22
C-N_o	0.80
C-Cl	0.39

Discussion

In Table VI, the results of the present investigations are compared with those of earlier works on the related compounds. About cyanuric chloride, the C-Cl distance (1.68 Å) is somewhat shorter than that of *sym*-trichlorobenzene (1.69 Å). On the C-N distance (1.33 Å), the same tendency is observed as compared with that of melamine (1.34 Å). We have not any accurate data to compare with the C-N_o distance (1.37 Å), but the inaccurate value (1.4 Å) for *p*-iodoaniline will serve to let us observe the similar tendency as the C-Cl distance of cyanuric chloride. Comparison of the bond order obtained above endorses these aspects.

TABLE VI

COMPARISON OF PARAMETER VALUES ON THE RELATED COMPOUNDS (Å)

Molecule				method	reference
Cyanuric chloride	C-N=1.33±0.02,	C-Cl=1.68±0.03,	$\angle$N-C-N=125±3°,.	E	
Melamine	C-N_r=1.34±0.01,	C-N_o=1.37±0.03,	$\angle N_r$-C-N_r=123±3°,.	E	
	C-N_r=1.33∼1.35,	C-N_o=1.35∼1.36,	$\angle N_r$-C-N_r=123∼125°,.	X	1
Cyanuric acid	C-N_r=1.36,			X	3
Cyanuric triazide	C-N_r=1.33,	C-N_o=1.50,	$\angle N_r$-C-N_r=137°,.	X	4
	C-N_r=1.31,1.38,	C-N_o=1.38.		X	5
Trisodium tricyan melamine trihydrate	C-N_r=1.34,1,35,	C-N_o=1.40,.		X	2
sym-Trichlorobenzene	C-C=1.41(assum.),	C-Cl=1,69±0.03,.		E	11
m,*p*-Dichlorobenzene	C-C=1.40(assum.),	C-Cl=1.69±0.03,.		E	11
Chlorobenzene	C-C=1.39±0.02,	C-Cl=1.69±0.03,.		E	11
p-Iodoaniline	C-C=1.4,	C-N=1.4_3,.		X	12

E indicates the electron diffraction method and X the X-ray diffraction method.

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[11] M.C. Sandorfy., *Bull. chim. phys.*, **16**, 615 (1949).

[12] L. O. Brockway and K. J. Palmer., *J. Am. Chem. Soc.*, 59, 2181 (1937).

[13] H. M. Powell, G. Huse and P. W. Cooke., *J. Chem. Soc.*, **1943**. 153

In the case of benzene derivatives, C-C distance of the ring is almost independent of the number or the species of the substituent. On the other hand, the cyanuric ring seemingly cannot stand invariably against the change of circumstances. The certificate of this phenomenon can be obtained also from the MO treatment. The bond order of cyanuric C-N_r distance is more easily affected by the introduction of new π-electron systems than that of benzene C-C distance as shown in Fig. 7. The distortion of the cyanuric ring from the regular hexagon, may be understood as the effect of a lone pair which is located on each N_r atom.

Summary

1. The molecular structure of cyanuric chloride and melamine were investigated by the electron diffraction. The following values were obtained by the analysis based on D_{3h} symmetry of the molecules: C-N_r=1.33±0.02 Å, C-Cl=1.68±0.03 Å, and $\angle N_r$-C-N_r=125±3° for cyanuric chloride: C-N_r=1.34±0.01 Å, C-N_0=1.37±0.03 Å, and $\angle N_r$-C-N_r=123±3° for melamine assuming N_o-H=1.04 Å, $\angle$C-N_o-H=$\angle$H-N_0-H=120°, and the coplanarity of all atoms.

2. Simple MO calculations were applied for both molecules as well as for *sym*-trichlorobenzene and *sym*-triaminobenzene. The resulted molecular diagrams were discussed together with the data obtained in the present experiment.

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