Molecular Structure of Acrylonitrile by Electron Diffraction

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The shortening of a single bond between two multiple bonds has been studied in various cases¹⁾, but not yet in the cases with the structure,

$$C=C-C\equiv N$$

The authors wish to report some results on acrylonitrile (Fig. 1) by the electron diffraction.

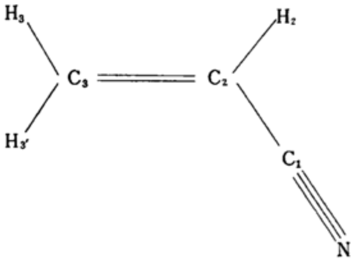

Fig. 1. Molecular scheme of acrylonitrile.

Experimental

The apparatus of electron diffraction is the same as in the previous reports from the authors' laboratory²⁾, with the exception of the use of two camera lengths, 9.1 and 10.1 cm. The electron wavelength, about 0.055 Å, was calibrated by gold foil diffraction.

The sample is kindly supplied to the authors' by Professor S. Kambara, b. p.=78°C.

Measurements were carried out by the usual visual method.

Procedure and Results

The experimental visual curve from eight photographs is shown in Fig. 2. The dotted line for $q>80$ means less accurate observation due to the obscurities of photographs and that for $q<10$ is an assumed line to help the calculation of the radial distribution curve.

The radial distribution curve has been calculated from the visual intensity curve according to the equation³⁾,

$$r\cdot D(r)=\sum_{q=1,2\cdots}^{q_{\max}} I(q)\exp(-aq^2)\sin\pi/10\cdot qr$$

$$q=(4\pi/\lambda)\sin(\theta/2)$$

$$\exp(-aq^2_{\max})=0.1$$

in which θ is the scattering angle, and λ is the wavelength of the beam. The curve obtained shows the still remaining ghosts. However, it is convenient to assign each peak in this curve for the following trial and error method.

The first peak of 1.16 Å is attributed to the C≡N bond from the consideration of weight**. The second peak of 1.38 Å corresponds to the overlapped contribution of C=C and C–C bonds. The peaks at 2.12 and 3.46 Å correspond to the interatomic distances of nonbonded C···H and C···N, respectively.

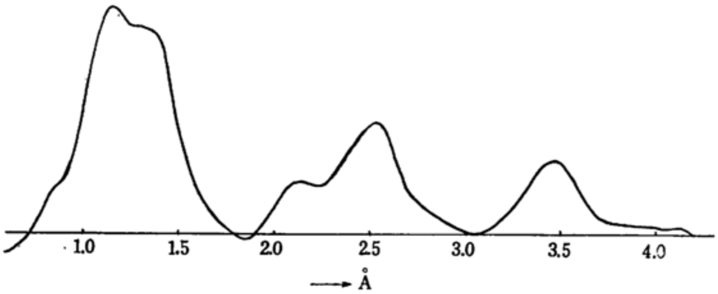

Fig. 2. Radial distribution curve.

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1) For example, see the following tables: L. E. Sutton and P. W. Allen, *Acta Cryst.*, **3**, 46 (1950); H. Oosaka, "Kagaku Jikkengaku", Vol. **5**, Kawade-Shobo, Tokyo (1943), p. 325; Y. Morino, K. Kuchitsu and Y. Hirota, "Jikken Kagaku Koza", Vol. 3, Maruzen Co., Ltd., Tokyo (1958), p. 241. The data for some molecules are given in Table III.

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

3) V. Schomaker et al., *J. Am. Chem. Soc.*, **64**, 2693 (1942).

** The term "weight" means the value of nZZ/r for each interatomic distance, where n is the number of the same interatomic distance r and Z is the atomic number.

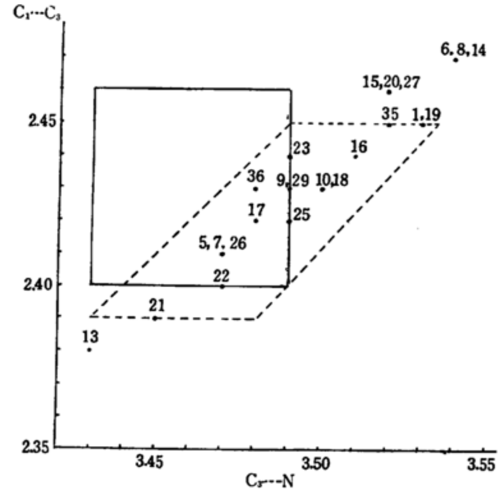

Fig. 3. The parameter chart of $C_1\cdots C_3$ vs. $C_3\cdots N$.

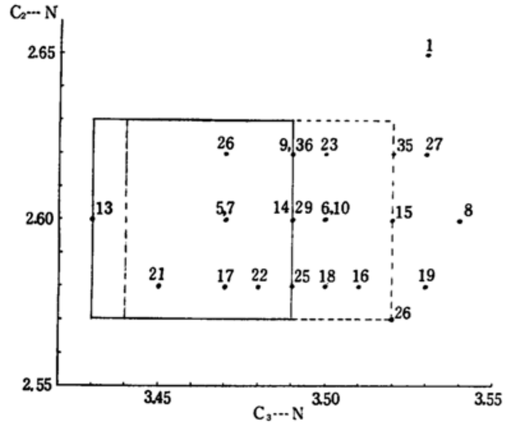

Fig. 4. The parameter chart of $C_2\cdots N$ vs. $C_3\cdots N$.

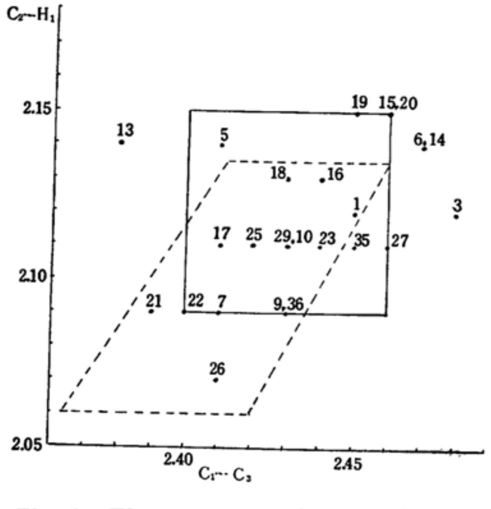

Fig. 5. The parameter chart of $C_2\cdots H_1$ vs. $C_1\cdots C_3$.

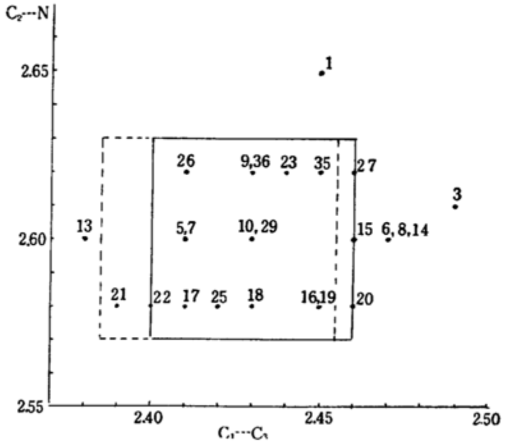

Fig. 6. The parameter chart of $C_2\cdots N$ vs. $C_1\cdots C_3$.

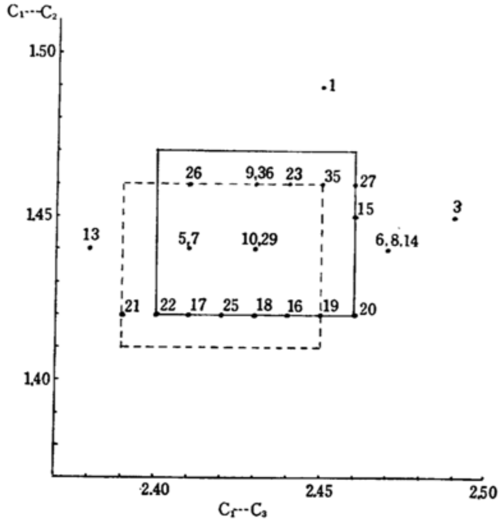

Fig. 7. The parameter chart of $C_1\cdots C_2$ vs. $C_1\cdots C_3$.

The theoretical intensity curve for assumed models has been calculated by the use of the equation[3]

$$I(q)=\sum_{ij}(Z_iZ_j/r_{ij})\exp(-a_{ij}q^2)\sin \pi/10\cdot qr_{ij}$$

$$a_{ij}=(\pi^2/200)l_{ij}$$

where r_{ij} is the distance between the i-th and j-th atom, Z_i is the atomic number of i-th atom and l_{ij} is the mean amplitude of r_{ij}.

The coefficient of thermal vibration, a_{ij}, is roughly estimated with reference to the calculated data [4-6]. The coefficients used

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[4] J. Karl, *J. Chem. Phys.*, **20**, 65 (1952).

[5] Y. Morino, K. Kuchitsu and T. Shimanouchi, ibid., **20**, 726 (1952).

[6] Y. Morino, K. Kuchitsu, A. Takahashi and K. Maeda, ibid., **21**, 1927 (1953).

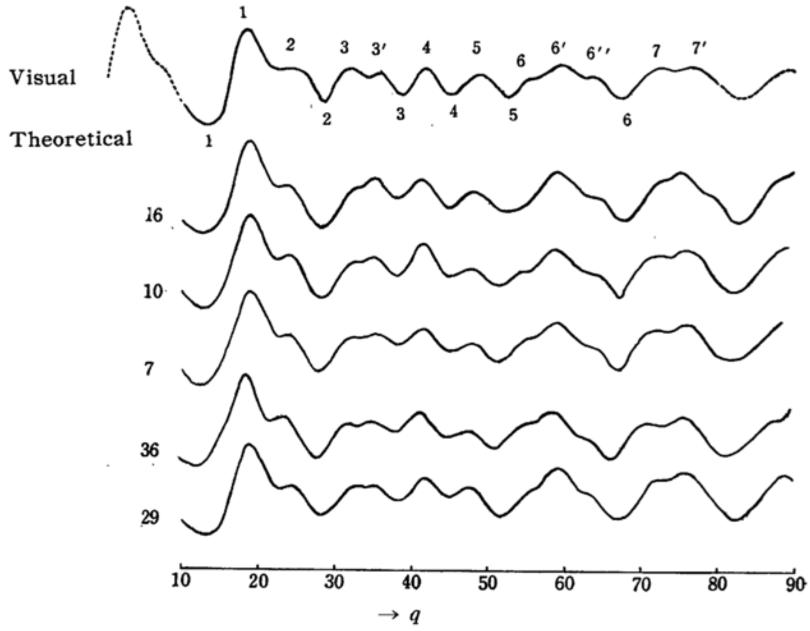

Fig. 8. Theoretical curves and visual curve.

TABLE I. THE COEFFICIENTS OF THERMAL VIBRATION

Atomic pair	a	Atomic pair	a
C—H	0.00028	$H\cdots C_1$	0.00013
C═C	0.00005	$C_2\cdots N$	0.00006
C—C	0.00008	$C_3\cdots N$	0.00012
C≡N	0	$H_3\cdots N$	0.00032
$H_3\cdots C_2$	0.00039	$H_2\cdots N$	0.00011
$C_3\cdots Cl$	0.00016		

TABLE II. THE COMPARISONS WITH EACH MODEL

Atomic pair	I	II	III	IV	V
C—C	1.42	1.44	1.44	1.46	1.44
C≡N	1.16	1.16	1.16	1.16	1.16
$C_1\cdots C_3$	2.44	2.43	2.41	2.43	2.43
$C_3\cdots N$	3.51	3.50	3.47	3.49	4.49
$C_2\cdots N$	2.58	2.60	2.60	2.58	2.60
Average of $q_{\text{calcd.}}/q_{\text{obsd.}}$	0.995	0.992	1.000	0.996	0.995
Root mean deviation	0.014	0.015	0.017	0.013	0.017

The length of atomic pair is given in Å unit.

are shown in Table I. The theoretical curve was calculated to cover the following ranges of parameters, $C_3{\equiv}N$ 1.16, $C_2{=}C_3$ 1.42∼1.46, $C_1\cdots C_3$ 2.41∼2.47 and $C_3\cdots N$ 3.46∼3.53 Å. In the above calculations, Z_H 1.25 and C—H 1.08 Å were used and each term of H···H was neglected. The theoretical curves, agreeing well with the visual intensity curve and having the values of parameters close to the interatomic distances obtained from the radial distribution curve, are shown in Fig. 2.

In Table II are shown the values of principal parameters in these models. Although these models are more appropriate rather than the others, the agreements with the visual curve are not sufficiently satisfactory. For example, there are considerable disagreements in the following aspects: (1) the relationships of intensity of max. 3 and 3′, (2) the relative intensity of max. 7 and 7′, (3) the location of min. 5 (the experimental has larger q than all the theoreical), (4) the relationships of intensity of max. 6, 6′ and 6′′. Therefore, it is difficult to prefer a model to the other form. However, the following ranges for the parameters may be supported in reference to values of the similar molecules (Table III), C≡N 1.15∼1.17, C═C 1.32∼1.36, C—C 1.42∼1.46 and $C_1\cdots C_3$ 2.41∼2.44 Å. The difficulty in determining the best model may be the result of the uncertain observation of intensity, especially in the range of larger q values.

However, it is probable from the considerations of the parameter charts that the molecule of acrylonitrile has the following interatomic distances:

C≡N	1.16±0.01 Å
C═C	1.34±0.02 Å
$C_2\cdots C_3$	2.43±0.02 Å
C—C	1.44±0.02 Å

TABLE III. THE INTERATOMIC DISTANCES (Å UNIT) OF SIMILAR COMPOUNDS

	Atomic pair					
Molecule	C≡N	C—C	C=C	C≡C	Method	Ref.
H—CN	1.156				M. W.*	1
$CH_3 \cdot CN$	1.157	1.458			M. W.	2
	1.16	1.49			E. D.**	3
CN·CN	1.16	1.37			E. D.	3
$CH_2=CH \cdot CH=CH_2$		1.46	1.35		E. D.	3
		1.47	1.37		S. P.***	4
$CH_3C \equiv C \cdot CH_3$		1.47		1.20	E. D.	3
$CH \equiv C \cdot C \equiv CH$		1.36		1.19	E. D.	3
$CH \equiv C \cdot CN$	1.157	1.382		1.203	M. W.	1
$CH_3 \cdot C \equiv C \cdot CH=CH_2$		1.42	1.35	1.20	E. D.	6
		1.47				

* M. W.; Microwave spectrum.
** E. D.; Electron diffraction.
*** S. P.; Infrared spectrum.

1) W. Gordy et al., *Phys. Rev.*, **86**, 1055 (1952).
2) L. F. Thomas et al., *Trans. Faraday Soc.* **51**, 619 (1955).
3) L. Pauling and L. O. Brockway, *J. Am. Chem. Soc.*, **61**, 927 (1939).
4) O. Bastianssen; these values were quoted from Sutton's Table., L. E. Sutton and P. W. Allen, *Acta. Cryst.*, **3**, 46 (1950).
5) A. A. Westenberg et al., *J. Am. Chem. Soc.*, **72**, 199 (1950).
6) V. Schomaker, *J. Am. Chem. Soc.*, **64**, 2693 (1942).

A further investigation about the structure of this molecule by the use of electron difraction sector microphotometer method will be given in succeeding paper***.

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*** During the preparation of this paper the authors read the following paper regarding the molecular structure of acrylonitrile; C. C. Costain and B. P. Stoiceff, *J. Chem. Phys.*, **30**, 777 (1959), which reported the following values about the interatomic distances, C≡N 1.1637, C—C 1.4256 and C=C 1.338_9 Å, by the use of microwave spectroscopy. The author's results are very near to their values.