1. Mayer, R., Daebritz, G., Ullrich, G., Werner, H., Ullricht, G. and Gewalt, K. *J. prakt. Chem.* **21** (1963) 80.
2. Jennings, T. J. (Shell Oil Co.) U.S.P. 3 265 712 (August 9, 1966); *Chem. Abstr.* **65** (1966) 12113.
3. Sharf, H. D. and Verbeek, M. *Angew. Chem.* **79** (1967) 870.
4. Jakobsen, H. J. and Lawesson, S.-O. *Tetrahedron* **23** (1967) 871 and refs. cited therein.
5. Mortensen, J. Z. and Lawesson, S.-O. *To be published.*
6. Nygaard, S.-P. and Lawesson, S.-O. *To be published.*
7. Lawesson, S.-O. *Arkiv Kemi* **11** (1957) 317.

Received March 28, 1968.

An Electron Diffraction Study of Tetracyanoethylene

HÅKON HOPE

Department of Chemistry, University of California, Davis, California 95616, U.S.A.

The crystal structure of monoclinic tetracyanoethylene (TCNE) was first reported by Bekoe and Trueblood.[1] They observed a rather short central C=C distance of 1.317 Å (e.s.d. 0.009 Å). Penfold and Lipscomb determined the structure of diaminomaleonitrile,[2] and found the C=C distance in that compound to be 1.363 Å (e.s.d. 0.004 Å). According to the discussion by these authors there seems to be no obvious reason for the C=C bonds to be so different in the two compounds. It was therefore felt to be of interest to study the structure of the TCNE molecule by the gas phase electron diffraction method.

Electron diffraction diagrams were recorded photographically with the sector method at nozzle to plate distances of about 12, 19, and 48 cm, using an electron wavelength of about 0.065 Å. The intensity data were treated in the usual manner,[3] giving a useful observed molecular intensity function for the range $s = 1.25$ Å^{-1} to $s = 55$ Å^{-1} from which a radial distribution curve was computed.

A planar, symmetric molecular model with C−C≡N linear was fitted to the radial distribution curve by adjusting structural parameters to give the closest possible correspondence between experimental and theoretical radial distribution curves.

Table 1. Tetracyanoethylene. Interatomic distances and root-mean-square amplitudes of vibration.

Atoms	Distance	R.m.s. amplitude
C(1)−C(2)	1.357 Å	0.046 Å
C(1)−C(3)	2.430	0.060
C(1)−N(4)	3.495	0.120
C(1)−C(9)	1.435	0.047
C(1)−N(10)	2.597	0.060
C(3)−N(4)	1.162	0.035
C(3)−C(5)	2.460	0.090
C(3)−N(6)	3.515	0.120
C(3)−C(7)	3.754	0.074
C(3)−N(8)	4.871	0.089
C(3)−C(9)	2.835	0.097
C(3)−N(10)	3.575	0.120
N(4)−N(6)	4.452	0.144
N(4)−N(8)	5.980	0.096
N(4)−N(10)	4.030	0.192
∠C(1)−C(2)−C(3)	121.1°	

The molecular dimensions and corresponding root-mean-square amplitudes of vibrations are listed in Table 1, with the numbering system indicated in Fig. 1.

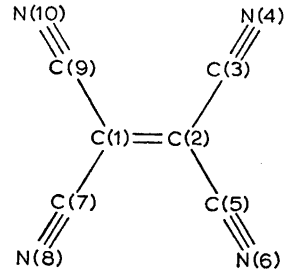

Fig. 1. Molecular model for tetracyanoethylene with indication of numbering system used.

The parameters in Table 1 were used in the calculation of the theoretical intensity curve shown in Fig. 2(*b*), and in the theoretical radial distribution curve in Fig. 3(*b*) (a damping function $\exp(-0.0009s^2)$ was used for the curves in Fig. 3).

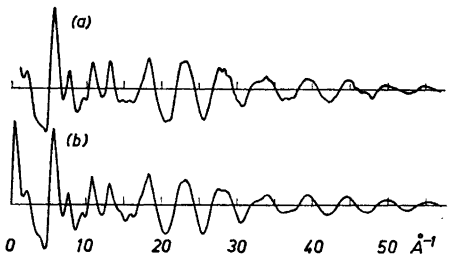

Fig. 2. (a) Experimental and (b) theoretical intensity curves for tetracyanoethylene.

Although it is difficult to accurately assess the errors in the determined interatomic distances, it is believed that the C≡N distance of 1.162 Å is accurate to within ±0.002 Å, and that the errors in the C=C bond (1.357 Å) and the C−C bond (1.435 Å) do not exceed 0.01 Å.

The results agree quite well with the distances found in diaminomaleonitrile (C=C 1.363 Å, C−C 1.438 Å, C−N 1.165 Å), and except for the C≡N distance are within the limits of error for corresponding distances in tetracyanoquinodimethane [4] (1.374, 1.441, 1.140 Å, respectively), and also for results obtained in a re-examination of the crystal structure of TCNE [5] which gave 1.339, 1.442, and 1.134 Å for the same three distances. It seems reasonable to conclude that the central C=C bond in TCNE actually is somewhat longer than the normal ethylenic double bond of 1.340 Å, in agreement with the view that the electron-withdrawing conjugative effect of the CN groups causes a depletion of electron density associated with the double bond, thereby lengthening this bond.

The experimental material on which this investigation is based has been sent to a member of the Oslo electron diffraction group who plans to refine the structure further through least-squares calculation.

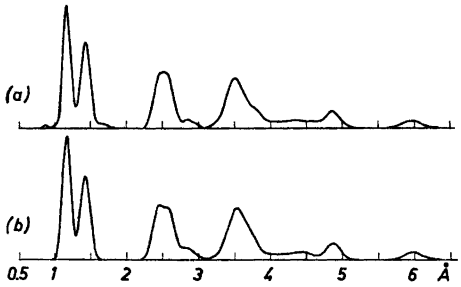

Fig. 3. (a) Experimental and (b) theoretical radial distribution functions for tetracyanoethylene.

Acknowledgements. The author is grateful to cand. real. A. Almenningen at the University of Oslo for preparing the electron diffraction diagrams, and to the University of Oslo Computing Facilities where most of the calculations were carried out.

1. Bekoe, D. A. and Trueblood, K. N. *Z. Krist.* **113** (1960) 1.
2. Penfold, B. R. and Lipscomb, W. N. *Acta Cryst.* **14** (1961) 589.
3. Almenningen, A., Bastiansen, O. and Fernholt, L. *Kgl. Norske Videnskab. Selskabs, Skrifter* **1955** No. 3.
4. Long, R. E., Sparks, R. A. and Trueblood, K. N. *Acta Cryst.* **18** (1965) 932.
5. Bekoe, D. A. and Trueblood, K. N. *Abstr. Meeting A. C. A. Bozeman, Montana*, p. 87.

Received February 2, 1968.