

luminous portions of the discharge, the rate being at a maximum in the negative glow. It is highly probable that positive ions are formed and propelled toward the cathode. Once outside the region of the discharge, the activated selenium combines with oxygen forming either the dioxide or trioxide; more trioxide is formed at higher activations of the selenium, as indicated by the effect of current and voltage on the per cent. of selenium trioxide in the product. The particles are positively charged, gas or wall neutralization taking place. Undoubtedly there is decomposition of selenium trioxide occurring. It seems logical that there will be less decomposition of a selenium trioxide particle if it is neutralized on the wall, which is at a low temperature and will take up the heat of neutralization. On the other hand, if gaseous neutralization takes place, the heat cannot be dissipated and therefore might decompose

the selenium trioxide molecule. It may be mentioned that only very low percentages of selenium trioxide were found when the tube was at room temperature during the reaction.

Summary

1. Banded deposits of selenium metal and selenium oxide were obtained in the glow discharge column. This afforded a means of determining the region in which the oxidation of selenium takes place. A correlation of voltage measurements and the character of the striated deposits shows that vaporization and activation of selenium takes place in the luminous regions. Combination with oxygen takes place in the dark regions.

2. After considering the experimental facts, a mechanism is suggested.

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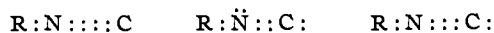
The CN Bond in Methyl Cyanide and Methyl Isocyanide

BY L. O. BROCKWAY

The bond between the carbon and nitrogen atoms in methyl cyanide and other organic nitriles has long been regarded as a triple electron pair bond, the structural formula for these compounds, $R-C\equiv N$, being considered satisfactory because in it carbon shows its normal valence of four and nitrogen one of its two normal valences, three. The isocyanides, on the other hand, according to the same considerations might have either one of two formulas, $R-N\equiv C$ and $R-N=C$. In the former the carbon atom is again quadrivalent while the nitrogen is quinquivalent; the latter formula is distinguished by the bivalent carbon atom. This formula, suggested by Nef, was favored because it was thought that the unusual chemical reactivity of the isocyanides was perhaps due to the "unsaturated" bivalent carbon atom.

In 1919 Langmuir¹ considered the possibility of a third formula for the CN radical on the basis of the Lewis theory of valency, namely, $R-C\equiv N$. Langmuir, however, noted the isosterism of cyanide ion and nitrogen molecule and rejected the triple bond structure because of the pronounced chemical differences between nitrogen molecule

and acetylene, for which a triple bond structure was accepted. He proposed a structure in which one pair of electrons was shared between the two atoms and the remaining eight formed an octet around the two atoms together. This structure was not generally accepted and Lewis in 1923² supported the validity of the triple bond formulation for the cyano radical. In accordance with the octet theory this formula originally considered by Langmuir is preferable to the first two mentioned above since it is the only one of the three in which each of the atoms is surrounded by four electron pairs. This is evident when the formulas are written to show both the shared and the unshared electrons, as follows



The interpretation of the octet theory by quantum mechanics in terms of the application of the Pauli exclusion principle to the elements of the first row of the periodic table still excludes the first but admits the second and third structures.

The first direct attempt to decide among these three bond types for methyl isocyanide was made

(2) G. N. Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., New York, 1923, p. 127.

(1) I. Langmuir, *THIS JOURNAL*, **41**, 868, 1543 (1919).

in 1930 by Lindemann and Wiegerebe,³ who concluded from a determination of the parachor that only the triple bond structure was correct. Hammick, New, Sidgwick and Sutton⁴ measured the parachor of ethyl isocyanide and decided on the same bond type. These authors also measured the dipole moment of several para-substituted aromatic cyanides and isocyanides. By a comparison of the moments they showed that the direction of the moment in the C-N link is different for the two classes of compounds; the nitrogen is negative with respect to the carbon in the cyanides and positive in the isocyanides. Nitrogen in isocyanide with a double bond would be negative but in the triple bond structure nitrogen has become positive by the loss of an electron to the carbon atom, the electron transfer being compensated energetically by the formation of the third electron pair bond. The positive nitrogen in the isocyanide accordingly supports the triple bond structure.

Dadiou,⁵ who regarded the foregoing evidence as "indirect," found support for the triple bond structures of both methyl cyanide and isocyanide in the Raman spectra of the two compounds. According to Dadiou every compound which is definitely known to contain a triple bond shows a strong Raman line in the range between 1960 and 2400 cm^{-1} . Each of these compounds shows a strong line in this region; therefore, each has a triple bond structure. Professor R. M. Badger of this Laboratory is making an analysis of the normal vibrations of these molecules in interpreting their infra-red absorption spectra. The evaluation of the force constants of the individual bonds will make the spectral evidence somewhat more satisfactory.

Another test for bond type in covalent compounds is found in the relation between bond type and internuclear distance. The bond distances for single, double and triple bonds are known quite accurately from the table of covalent radii

due to Pauling and Huggins.⁶ The distances for bonds of intermediate types are known from investigations⁷ of the effect of resonance on bond distances.

In the present investigation I have measured the internuclear distances in methyl cyanide and isocyanide by electron diffraction of the vapors. The experimental procedure and methods of interpreting the diffraction patterns have been described in detail.⁸

Methyl Cyanide.—Eastman methyl cyanide was fractionated and a sample boiling at 80.4–80.5° (uncorr.) was used at room temperature for the electron diffraction. The camera distance was 10.85 cm. and the electron wave length was 0.0611 Å. The photographs show five rings of a very characteristic appearance. The first is strong and

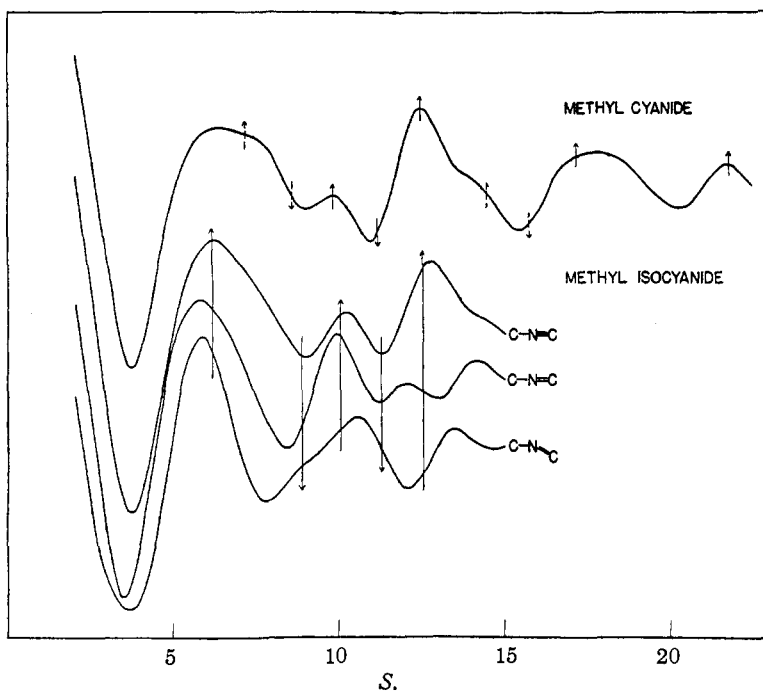


Fig. 1.—Theoretical electron diffraction curves for methyl cyanide and isocyanide with the positions of the maxima and minima measured on the photographs indicated by arrows.

diffuse, the second weak and sharp, the third strong and sharp with a shelf on the outside edge, the fourth diffuse and the fifth sharp. Reproducible measurements of the diameters could be made only on the sharp rings, *i. e.*, the second, fourth and fifth.

The theoretical curve (Fig. 1) was calculated for a linear arrangement of two carbon atoms and a nitrogen atom with distances of 1.54 and 1.16 Å. for the carbon-carbon and carbon-nitrogen bonds, respectively. The distance 1.06 Å. was used for the carbon-hydrogen bonds in the

(3) H. Lindemann and L. Wiegerebe, *Ber.*, **63**, 1650 (1930).

(4) D. L. Hammick, R. C. A. New, N. V. Sidgwick and L. E. Sutton, *J. Chem. Soc.*, 1876 (1930).

(5) A. Dadiou, *Ber.*, **64B**, 358 (1931).

(6) L. Pauling and M. L. Huggins, *Z. Krist.*, **87**, 224 (1934).

(7) L. Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293 (1932); L. Pauling, L. O. Brockway and J. Y. Beach, *This Journal*, **67**, 2705 (1935).

(8) L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

methyl group, with H-C-H angles of $109^{\circ}28'$. The linear configuration is supported by the known linear form of HCN⁹ and by preliminary results of the analysis of the infra-red absorption spectrum of methyl cyanide now in progress. Non-linear models were not considered.

The characteristic qualitative features observed in the photographs are well reproduced in the curve. The positions of the observed maxima and minima are indicated by the arrows; the points which did not afford reproducible measurements are shown by dashed arrows and were not used in the quantitative comparison in Table I. The final values observed, $1.54 \pm 0.02 \text{ \AA.}$ and $1.16 \pm 0.02 \text{ \AA.}$, are exactly those for a single carbon-carbon bond and a triple carbon-nitrogen bond, respectively.

TABLE I
METHYL CYANIDE

Max.	Min.	<i>s</i> , obsd.	<i>s</i> , calcd. for C-C = 1.54 and C-N = 1.16	C-C, \AA.	C-N, \AA.
1		7.19	(6.20)		
	2	8.60	9.00	(1.613)	
2		9.84	9.78	1.530	1.152
	3	11.17	10.88		
3		12.44	12.43	1.539	1.159
Shelf		14.53			
	4	15.75	15.40	1.507	1.135
4		17.16	17.65	1.584	1.193
5		21.77	21.68	1.533	1.155
			Average	1.539 \AA.	1.159 \AA.
			Av. dev.	0.018	0.014

Final value: C-C = $1.54 \pm 0.03 \text{ \AA.}$; C-N = $1.16 \pm 0.02 \text{ \AA.}$

Methyl Isocyanide.—Methyl isocyanide was prepared by Dr. C. E. Wilson using methylamine, chloroform, and alcoholic potash. The electron diffraction photographs were taken with a camera distance of nearly 20 cm. and the three rings observed covered the negative. Of these three rings the third is considerably stronger than the second although weaker than the first.

Three molecular models were considered. The first corresponds to the triple bond structure of isocyanide and is linear (except for the hydrogen atoms). The second is also linear but has the double bond N-C distance, 1.31 \AA. For the third model a CNC angle of 125° was chosen with the double bond distance since the angle between a single and a double bond is usually observed to have about this value.

The second and third models are quite definitely eliminated. The third maximum in these curves is weaker than the second whereas it is observed to be stronger. In the case of the third curve the second and third maxima both appear to be somewhat asymmetric but in the photographs they are sharply defined. The positions of the outer rings are not correct in either curve as indicated by the arrows showing the observed *s* values.

Model I corresponding to a single and a triple bond in the molecule shows good qualitative and quantitative agreement with the photographs. The quantitative com-

parison of Table II leads to a CH₃-N distance of $1.48 \pm 0.03 \text{ \AA.}$ and a N-C distance of $1.17 \pm 0.02 \text{ \AA.}$

TABLE II
METHYL ISOCYANIDE

Max.	Min.	<i>s</i> , obsd.	<i>s</i> , calcd. for C-N = 1.46 and N-C = 1.16	CH ₃ -N, \AA.	N-C, \AA.
1		6.17	6.24	1.476	1.173
	2	8.88	9.00	1.480	1.176
2		10.04	10.21	1.485	1.180
	3	11.27	11.26	1.459	1.159
3		12.51	12.73	1.485	1.180
			Average	1.477 \AA.	1.173 \AA.
			Av. dev.	0.008	0.006

Final value: CH₃-N = $1.48 \pm 0.03 \text{ \AA.}$; N-C = $1.17 \pm 0.02 \text{ \AA.}$

Discussion.—The bond distances for single, double and triple carbon-nitrogen bonds are 1.47, 1.32 and 1.16 \AA., respectively. The distance 1.16 \AA. observed in methyl cyanide supports the triple bond structure and the structure represented by the formula CH₃-C≡N: is now well substantiated.

The observed distance of 1.17 \AA. in the isocyanide is also very close to the triple bond distance, but the apparent discrepancy of 0.01 \AA. suggests the possibility of resonance with the double bond structure. A 60% contribution of this structure would increase the observed bond distance by only 0.02 \AA. above the value for a triple bond so that the double bond structure may well be important in the normal state of the isocyanide molecule. The linear configuration indicates, however, that the triple bond structure predominates in determining the properties of methyl isocyanide.

I wish to thank Dr. Chester Wilson for the preparation of the isocyanide and Professor Linus Pauling for his kindly criticism of the investigation.

Summary

The electron diffraction determination of the molecular structures and bond distances of methyl cyanide and isocyanide shows that a triple bond exists in the cyano group of each compound. The observed distances in the first are CH₃-C = $1.54 \pm 0.02 \text{ \AA.}$, C-N = $1.16 \pm 0.02 \text{ \AA.}$; in the second CH₃-N = $1.48 \pm 0.03 \text{ \AA.}$, N-C = $1.17 \pm 0.02 \text{ \AA.}$ Both compounds are linear except for the hydrogen atoms.

(9) R. Badger and J. Binder, *Phys. Rev.*, **37**, 800 (1931).