

also account for the observed inversion of Λ_0 values for Bu_3HNPI and Bu_4NPI .

It has been known for some time⁷ that aniline picrate exists in two forms with different solubilities, but no account of electrical properties has been published.⁸ Pedersen suggested that the two forms might be molecular addition compound and electrolyte, but in view of the color change which occurs⁹ when "organic nitro compounds form addition products with aromatic molecules" was inclined to doubt the hypothesis. The present work, however, clearly shows that these picrates exhibit electrical anomalies, which easily can be accounted for by the assumption of two isomeric structures, which differ in the location of a proton. Further work, suggested by the present data, is planned.

Another group of electrolytes has been long known, which exhibit a similar behavior. The heavy metal cyanides in liquid ammonia¹⁰ have

(7) K. J. Pedersen, *THIS JOURNAL*, **56**, 2615 (1934).

(8) An abnormally low conductance of aniline picrate in nitrobenzene has been observed. The conductance was greatly increased by adding either amine or picric acid, which indicates the displacement of an equilibrium, and is excellent evidence in favor of the existence of a molecular compound. We are indebted to Dr. C. A. Kraus of Brown University for this information.

(9) Pfeiffer, "Organische Molekülverbindungen," 1922, pp. 218-245.

(10) Franklin and Kraus, *THIS JOURNAL*, **27**, 197 (1905).

low equivalent conductances, which are nearly independent of concentration over a wide range of dilution. It is obvious that the assumption of polar and non-polar isomers for these compounds could account for the experimental facts.

Summary

1. The conductances at 40° and 60 cycles in tricresyl phosphate of the following salts have been determined: tetrabutyl-, tributyl-, tribenzyl-ammonium, *p*-phenylaniline-, dimethylaniline and aniline picrates, and lead abietate.

2. Tetrabutyl- and tributylammonium picrates give practically normal conductance curves. Two anomalies appear, however: the product of limiting equivalent conductance and viscosity for the tetra salt in tricresyl phosphate is about 30% larger than for the same salt in ethylene chloride, and the conductance curve satisfies the equations derived on the basis of a simple binary ionic association over an unexpectedly wide range of concentration.

3. The picrates of the aromatic amines and lead abietate give conductance curves which suggest that they exist in two modifications, one of which cannot furnish ions.

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The Electron Diffraction Investigation of the Molecular Structures of Cyanogen Chloride and Cyanogen Bromide

BY J. Y. BEACH¹ AND ANTHONY TURKEVICH²

The decrease of interatomic distances below the values expected from the table of covalent radii^{3,4} has been observed in several compounds.^{5,7} This shortening has been discussed in terms of multiple bond character and the resonance of molecules among several electronic structures.^{4,8} It seemed to us possible that this effect might also be observed in the case of the cyanogen halides, ClCN and BrCN . To investigate this we have

(1) National Research Council Fellow in Chemistry.

(2) Cramer Fellow from Dartmouth College.

(3) Pauling and Huggins, *Z. Krist.*, (A) **87**, 205 (1934).

(4) Pauling and Brockway, *THIS JOURNAL*, **59**, 1223 (1937).

(5) Brockway and Wall, *ibid.*, **56**, 2373 (1934).

(6) Brockway and Beach, *ibid.*, **60**, 1836 (1938).

(7) Gregg, Hampson, Jenkins, Jones and Sutton, *Trans. Faraday Soc.*, **33**, 852 (1937).

(8) Pauling, Brockway and Beach, *THIS JOURNAL*, **57**, 2705 (1935).

determined the interatomic distances in these molecules by electron diffraction.

The apparatus used was that described by Beach and Stevenson.⁹ The electrons were accelerated by 41 kilovolts and their wave length, 0.0590 Å., was determined accurately from transmission pictures of gold foil ($a_0 = 4.070$ Å.). The diffraction patterns were recorded on photographic plates 12.19 cm. from the nozzle. The interpretation of the diffraction pattern was carried out by the visual method¹⁰ as well as by the radial distribution method¹¹ and a modification of the latter.¹²

(9) Beach and Stevenson, *J. Chem. Phys.*, **6**, 75 (1938).

(10) Pauling and Brockway, *ibid.*, **2**, 867 (1934).

(11) Pauling and Brockway, *THIS JOURNAL*, **57**, 2684 (1935).

(12) Degard, *Bull. soc. sci. Liège*, **2**, 115 (1938); Schomaker, *THIS JOURNAL*, to be published.

Although chemical evidence has not been conclusive in regard to the structure of the cyanogen halides,¹³ the weight of the physical evidence seems to favor the formula XCN rather than XNC. Studies of the ultraviolet absorption¹⁴ by these compounds show them all to possess the same structure. Consideration of the bond energies involved¹⁴ and of the Raman vibrational frequencies¹⁵ point definitely to the structure XCN. Similarly, the assumption of a linear arrangement of atoms in a group involving a triply bonded carbon atom is supported by the experimentally determined linear configurations of HCN,¹⁶ (CN)₂,¹⁷ and by the zero dipole moment of *p*-dicyanobenzene.¹⁸ For these reasons only molecular structures involving a linear arrangement of the atoms in an XCN structure were considered in calculating the theoretical intensity curves.

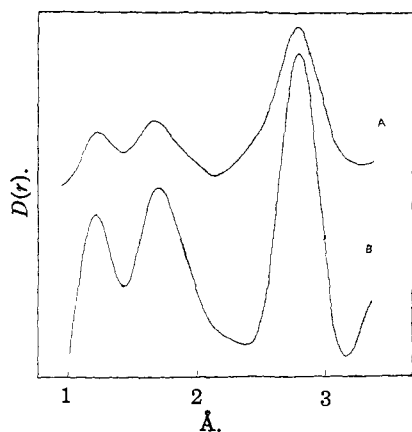


Fig. 1.—Cyanogen chloride: curve A, ordinary radial distribution function; curve B, modified radial distribution function.

Cyanogen Chloride.—The cyanogen chloride was prepared by the method of Vanino.¹⁹ The product was purified by fractional distillation in a vacuum system. The sample holder was a one-liter flask in which the sample was stored as a gas at 300 mm. The photographs showed eight maxima. The last one was too faint to measure with certainty. The visually estimated intensi-

ties and the observed values of $s (= (4\pi \sin \theta/2)/\lambda)$ are given in Table I.

TABLE I
CYANOGEN CHLORIDE

Max.	Min.	<i>l</i>	<i>s</i> _{obsd.}	<i>s</i> _{calcd.}	<i>s</i> _{calcd./s_{obsd.}}
1		8	2.893	2.50	(0.864)
	2		3.997	3.57	(.893)
2		20	5.075	4.93	.971
	3		6.389	6.17	.966
3		15	7.371	7.43	1.008
	4		8.497	8.50	1.000
4		8	9.514	8.95	0.941
	5		10.75	10.38	0.966
5		12	11.74	11.85	1.009
	6		13.03		
6		3	13.87		
	7		15.27	14.70	0.963
7		6	16.34	16.10	0.985

Average 0.979

Results: C—Cl = 1.65 Å.

C—N = 1.13 Å.

^a From curve D, Fig. 3.

The radial distributions of scattering matter in the molecule, as obtained by the ordinary¹¹ and modified¹² radial distribution methods, is shown in Fig. 1. Both curves possess three maxima corresponding to the carbon-nitrogen, the carbon-chlorine, and the nitrogen-chlorine distances, respectively. The maxima on the unmodified curves are located at 1.24, 1.67, and 2.78 Å. The maxima on the modified curve are at 1.22, 1.71, and 2.79 Å. Because the carbon-nitrogen term in the scattering function is the smallest, the carbon-nitrogen distance is the least certain. A better value for this distance can be obtained from the radial distribution functions by making the assumption that the molecule is linear and subtracting the average carbon-chlorine distance, 1.69 Å., from the average nitrogen-chlorine distance 2.79 Å., giving 1.10 Å. instead of 1.23 Å. The best value, however, will be obtained from the visual method.

Having made the assumption that the molecule is linear there is only one shape parameter to be varied in calculating the theoretical curves. That is the ratio of the carbon-chlorine distance to the carbon-nitrogen distance. We have calculated theoretical curves for seven models, varying this ratio from 1.80/1.15 to 1.56/1.15. These curves are shown in Fig. 3. Most of the models can be eliminated from a qualitative comparison with the photographs. The fourth maximum on the photographs is less intense than the third or the fifth and its outside minimum is much deeper

(13) See, for example, Taylor and Baker in Sidgwick, "Organic Chemistry of Nitrogen," Oxford University Press, New York, 1937, pp. 326-328.

(14) Badger and Woo, *THIS JOURNAL*, **53**, 2572 (1931).

(15) West and Farnsworth, *J. Chem. Phys.*, **1**, 402 (1933).

(16) Barker and Choi, *Phys. Rev.*, **42**, 777 (1932).

(17) Brockway, *Proc. Natl. Acad. Sci.*, **19**, 868 (1933).

(18) Weissberger and Sängewald, *J. Chem. Soc.*, 855 (1935).

(19) Vanino, "Präparative Chemie," II Band, Organische Teil, Dritte Auflage.

than the minimum to the inside. This rules out F and G. Models A and B can be ruled out from an inspection of the sixth maximum. This, on the photographs, appears in relation to the fifth and seventh much as the fourth maximum appears in relation to the third and the fifth. Models A and B are unsatisfactory because the sixth maximum is too symmetrically located with respect to the fifth and the seventh. As the most probable model we have taken D. Quantitative comparison of curve D with the photographs is made in Table I. These values, taken with the radial distribution function, lead to the final results: carbon-chlorine distance, 1.67 ± 0.02 Å.; carbon-nitrogen distance, 1.13 ± 0.03 Å.

Cyanogen Bromide.—Cyanogen bromide was prepared as recommended in "Organic Syntheses."²⁰ The product consisted of white crystals. The photographs, taken with the sample at 25° , showed eight rings. The visually estimated intensities and the observed values of s ($=4\pi \sin \theta/2/\lambda$) are given in Table II.

TABLE II
CYANOGEN BROMIDE

Max.	Min.	l	$s_{\text{obsd.}}$	$s_{\text{calcd.}}^a$	$s_{\text{calcd.}}/s_{\text{obsd.}}$
1		8	2.793	2.62	(0.938)
	2		3.832	3.37	(.879)
2		20	4.861	4.57	.940
	3		6.044	5.82	.963
3		15	7.000	7.10	1.014
	4		8.152		
4		8	8.964		
	5		10.22	9.80	0.959
5		12	11.25	11.17	.993
6		4	13.40	13.35	.996
7		4	15.37	15.03	.978
8		2	17.93	17.61	.982
Average					.978
Results: C-Br = 1.79 Å.					
C-N = 1.13 Å.					

^a From curve D, Fig. 4.

The radial distribution of scattering matter in the molecule, as determined by the ordinary¹¹ and modified¹² radial distribution methods, is shown in Fig. 2. The maxima in each case correspond to the carbon-nitrogen, the carbon-bromine, and the nitrogen-bromine distances, respectively. In the unmodified curve these are located at 1.31, 1.78, and 2.92 Å. The maxima on the modified curve appear at 1.27, 1.80, and 2.93 Å. The first peak is not reliable because the carbon-nitrogen term contributes but little to the

(20) "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., Vol. XI, 1931.

total scattering. The distance may be estimated more accurately by assuming that the molecule is linear and subtracting the carbon-bromine distance, 1.79 Å., from the nitrogen-bromine distance, 2.93 Å. This result of 1.14 Å. is close to the final value obtained from the visual method.

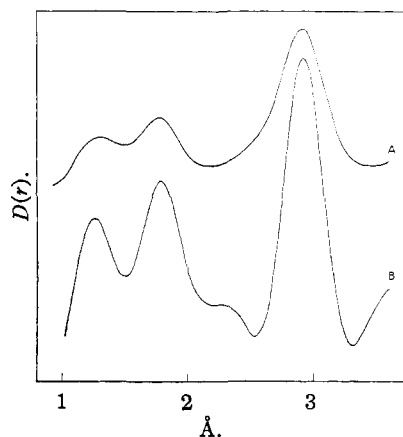


Fig. 2.—Cyanogen bromide: curve A, ordinary radial distribution function; curve B, modified radial distribution function.

As in the case of the chloride, the molecule has only one shape parameter, the ratio of the carbon-bromine distance to the carbon-nitrogen distance. We have calculated seven theoretical intensity curves varying this ratio from 1.95/1.15 to 1.71/1.15. These curves are shown in Fig. 4. A qualitative comparison of these curves with the photographs shows most of the models to be unsatisfactory. Models F and G are ruled out because the fourth maximum, which appears as a shelf on the outside of the third, is too high. The seventh maximum in the photographs is as high or is higher than the sixth. Models A and B are unsatisfactory in this respect. In addition they do not possess a high enough fourth maximum. Curve D was taken as the one most closely resembling the photographs. Quantitative comparison of the photographs with curve D is made in Table II. These results and the radial distribution curves lead to the final values for the distances: carbon-bromine, 1.79 ± 0.02 Å.; carbon-nitrogen, 1.13 ± 0.04 Å.

Discussion.—The value found for the carbon-chlorine bond distance in cyanogen chloride is 1.67 Å. This is 0.09 Å. less than the sum of the single covalent radii³ for carbon and chlorine, 1.76 Å. From an inspection of the structure of

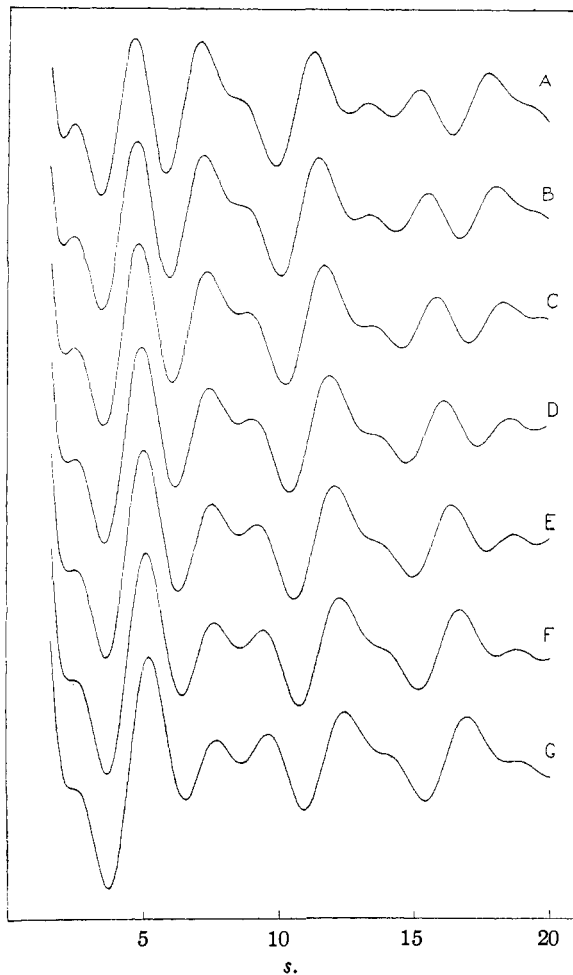
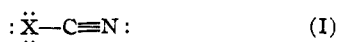


Fig. 3.—Theoretical intensity curves for cyanogen chloride. The ratios of the carbon-chlorine to the carbon-nitrogen distances are: for curve A, 1.80/1.15; curve B, 1.76/1.15; curve C, 1.72/1.15; curve D, 1.68/1.15; curve E, 1.64/1.15; curve F, 1.60/1.15; curve G, 1.56/1.15.

cyanogen chloride, it is evident that in addition to the conventional electronic structure



it is possible to write another



Structure II has the same number of covalent bonds as I, but is energetically less satisfactory because it involves a separation of charge. The extent to which structure II contributes to the actual configuration of the molecule is determined by the observed bond distance. As has been pointed out,⁸ the shortening of a single bond due to partial double bond character is much greater than the lengthening of the triple bond distance

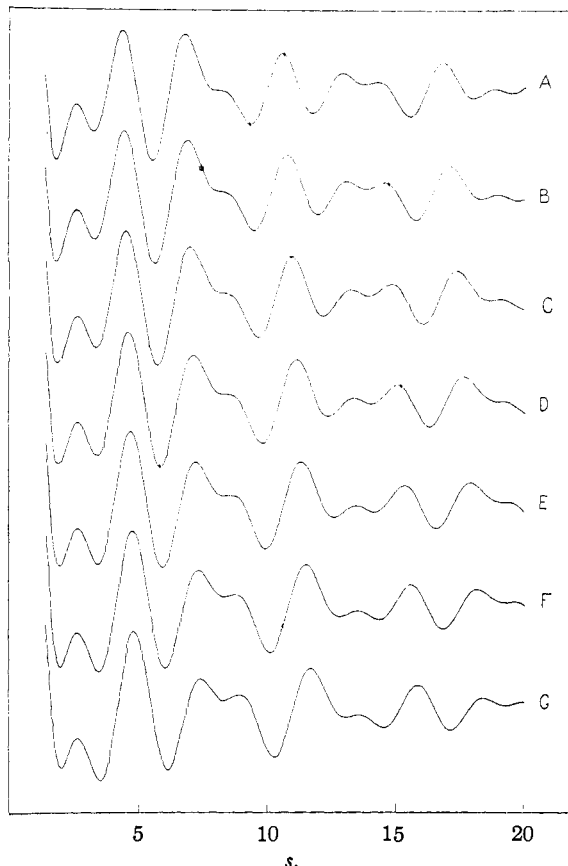


Fig. 4.—Theoretical intensity curves for cyanogen bromide. The ratios of the carbon-bromine to the carbon-nitrogen distances are: for curve A, 1.95/1.15; curve B, 1.91/1.15; curve C, 1.87/1.15; curve D, 1.83/1.15; curve E, 1.79/1.15; curve F, 1.75/1.15; curve G, 1.71/1.15.

due to partial double bond character. For this reason, and because the carbon-chlorine distance is known more accurately than the carbon-nitrogen distance, we shall use only the carbon-chlorine distance in estimating the extent to which the second structure contributes to the actual structure of the molecules. We assume that the shape of the curve relating bond distance to bond character is the same for the carbon-chlorine bond as for the carbon-carbon bond. Taking this curve⁴ and using 1.76 Å. as the single bond distance, and putting 1.57 Å. for the double bond distance,⁴ we find that the percentage double bond character for a carbon-chlorine bond whose distance is 1.67 Å. is 24%.

This calculation has been repeated for cyanogen bromide. The same assumptions were made and the same procedure was followed as in the case of the chloride. The double bond radius of bromine was taken to be 1.04 Å. The double bond

character of the carbon-bromine bond in cyanogen bromide was found to be 33%.

The contribution of structure II to the actual structure is 24% for cyanogen chloride and 33% for cyanogen bromide. That structure II should contribute more in the case of the bromide than in the case of the chloride is to be expected from the electronegativities. Chlorine is more electronegative than bromine. Therefore structure II, which imposes a positive formal charge on the halogen, would be less favorable for the chloride than for the bromide.

The relation found between bond distances and vibration frequencies²¹ suggests that the stretching force constants for the carbon-chlorine bond in cyanogen chloride would be greater than that for a normal single carbon-chlorine bond. This is found to be the case. The force constant for the carbon-chlorine bond in carbon tetrachloride²² is 0.4 megadyne/cm., while in cyanogen chloride it is 0.5 megadyne/cm.²³

Dipole moment measurements of the cyanogen halides have not been made yet. If no resonance occurred, the moments would be expected to be

(21) Badger, *J. Chem. Phys.*, **2**, 128 (1934).

(22) Voge and Rosenthal, *ibid.*, **4**, 137 (1936).

(23) Linnet and Thompson, *Nature*, **139**, 509 (1937).

the difference between the C≡N and the C—Cl bond moments. The C≡N moment is greater than the C—Cl moment and so the resultant would be toward the N. Structure II has a large moment toward the N due to the separation of a charge. Because of the resonance, therefore, the moments of the molecules should be greater than the difference between the C≡N and the C—X bond moments. This effect of resonance on the dipole moment has already been noticed in the case of molecules similar to the cyanogen halides, namely, in the chloro and cyano derivatives of acetylene.²⁴

Summary

The molecular structures of cyanogen chloride and cyanogen bromide have been investigated by electron diffraction. The molecules were assumed to be linear nitriles. The results for the chloride are: carbon-chlorine 1.67 ± 0.02 Å.; carbon-nitrogen 1.13 ± 0.03 Å. The results for the bromide are: carbon-bromine 1.79 ± 0.02 Å.; carbon-nitrogen 1.13 ± 0.04 Å. The double bond character of the carbon-halogen bond is 24% in the chloride and 33% in the bromide.

(24) Curran and Wenzke, *THIS JOURNAL*, **59**, 943 (1937).

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Internal Rotation in Ethylene Chlorobromide and Ethylene Bromide

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Introduction

In a recent² paper the molecular structure of ethylene chloride was investigated by the electron diffraction method in order to determine the extent of internal rotation about the carbon-carbon bond. It was shown that there is a high potential barrier to such internal rotation. The configuration with the lowest internal potential energy is the *trans* configuration and the height of the barrier is between 5 kcal./mole and infinity. An attempt to duplicate this potential curve was then made by calculating the exchange repulsions and electrostatic interactions of the six atoms at the ends of the molecule. The potential curve obtained by adding these terms together was used to calculate a theoretical intensity of scattering

curve, assuming a Boltzmann distribution of molecules among all possible configurations. This curve did not agree with the electron diffraction photographs of ethylene chloride. In order to obtain a potential function compatible with the electron diffraction data it was necessary to re-evaluate the chlorine-chlorine exchange repulsions. The Morse curve for use in calculating the chlorine-chlorine repulsions was obtained² from the observed Morse curve by multiplying by 14/8. The chlorine-chlorine repulsions obtained using this Morse curve lead to a corrected potential barrier. The theoretical intensity curve for this corrected potential function was in agreement with the electron diffraction photographs.

In the present investigation we have undertaken to determine the potential barrier to internal rotation in ethylene chlorobromide and ethyl-

(1) National Research Fellow in Chemistry.

(2) Beach and Palmer, *J. Chem. Phys.*, **6**, 639 (1938).