THE ELECTRON-DIFFRACTION INVESTIGATION OF THE MOLECULAR STRUCTURE OF CYANOGEN AND DIACETYLENE (WITH A NOTE ON CHLORINE DIOXIDE)*

BY L. O. BROCKWAY

GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY

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The structures of cyanogen and diacetylene have been previously investigated by the electron-diffraction method by Wierl,[1] who reported non-linear models with 150° bond angles for both molecules. The improbability of this conclusion, which is incompatible with all other evidence for the angle between a triple and a single bond on the same carbon atom, led to a reinvestigation of these compounds by the electron-diffraction method.

The models for which theoretical intensity curves were calculated were chosen from a consideration of the electronic structures corresponding to low energy values for the molecule. Those for cyanogen may be represented as follows:

$$:N:::C:C:::N: \qquad I$$

$$:\overset{\cdot}{N}::C::C::\overset{\cdot}{N}: \qquad II$$

$$:\overset{\cdot}{N}::C::C::\overset{+}{N}: \qquad III$$

$$\overset{+}{:N}::C::C::\overset{\cdot-}{N}: \qquad IV.$$

The probable atomic configurations may be chosen on the basis of Pauling's[2] discussion of resonance between Lewis electronic structures. The contribution of I to the resonating structure is as important as that of any single structure above because of the two strong bonds which it contains; therefore, the only necessary consideration is the effect of combining the others with I. II, III and IV would tend to decrease the carbon-carbon distance toward that of a double bond. Of these three II is the most important because each atom is electrically neutral and the molecule has a lower energy value than III or IV has.

Four theoretical intensity curves have been calculated, in which the ratio of carbon-carbon to carbon-nitrogen distance has the values 1.54/1.16, 1.46/1.16, 1.42/1.16 and 1.38/1.16. In the figures the curves are designated with the numerators of these fractions. The first corresponds to I alone, the fourth to complete resonance of I with the others, and the second and third to two stages of partial resonance. The most important qualitative feature of these curves is the disappearance of the second maximum in going from the first to the fourth curve.

The photographs of cyanogen are characterized by a sharp first ring with
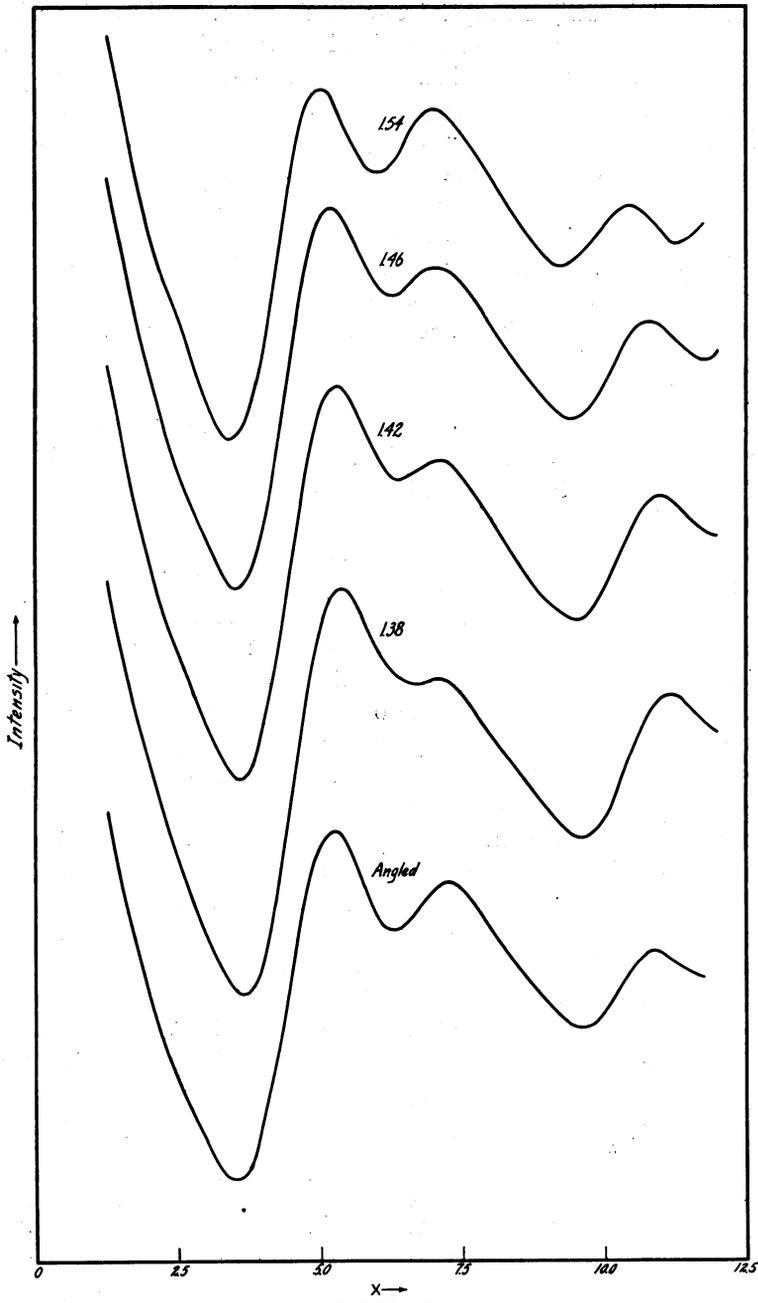
FIGURE 1

Theoretical intensity curves for cyanogen.

a broad "shelf" slowly falling off toward the outside edge. This is followed further out by a maximum which is sharply defined on both sides. This qualitative appearance eliminates the single-bond model I since the result of the investigation of sulphur hexafluoride[3] indicates that such a double maximum is duplicated in the appearance of the photograph.

The reproductions of the photographs obtained by Wierl show the same characteristics and lead to the elimination of the same model. His unwillingness, however, to alter the two bond distances from the chosen values, 1.52 and 1.20, led him to relinquish the linearity of the molecule and to assume an angle of 150° between the carbon-carbon and carbon-nitrogen bonds, and he claimed thereby to find satisfactory agreement with the photographs.

Three objections must be brought against the conclusion of Wierl. The first is that in no other case has a compound containing a triple-bonded carbon atom been measured by any method and found to have the single bond not in a straight line with the triple bond. The second is that in view of the resonance possibilities suggested by Pauling and for which additional evidence is furnished by the results of this investigation there is no need to consider non-linear models. The third objection is to be found in the appearance of the fifth curve in the illustration. In this the second maximum is only a little less prominent than in the first curve. The fifth curve was calculated from the 150° model but using the bond distances 1.54 and 1.16 taken from the table of covalent radii.[2] The discrepancy with Wierl's curve is probably due to his use of somewhat different bond distances which appear to correspond to the case of diacetylene. His use of the same curves for cyanogen and diacetylene is open to the objection that it neglects the difference between the carbon-nitrogen and carbon-carbon triple-bond distances in the two compounds. This leads to different values for the central carbon-carbon bond distances in the two compounds, a result which is highly improbable because of the identical electronic arrangement. Wierl's support of the model with the 150° angle is, therefore, the result of incorrect interpretation of the photographs.

The quantitative comparison of the photographs is shown in the following table:

TABLE 1

	$\frac{\text{SIN } \theta/2}{\lambda}$	1.46		1.42		1.38	
		x	a	x	a	x	a
1st min.	0.352	4.77	1.08	4.85	1.10	4.88	1.10
1st max.	0.427	6.45	1.20	6.55	1.22	6.63	1.24
2nd min.	0.718	10.63	1.18	10.82	1.20	10.85	1.21
2nd max.	0.831	12.03+	1.15	12.23	1.17	12.45	1.19

The values in the first column are the averages from two photographs. The x-values are taken from the theoretical curves for the respective
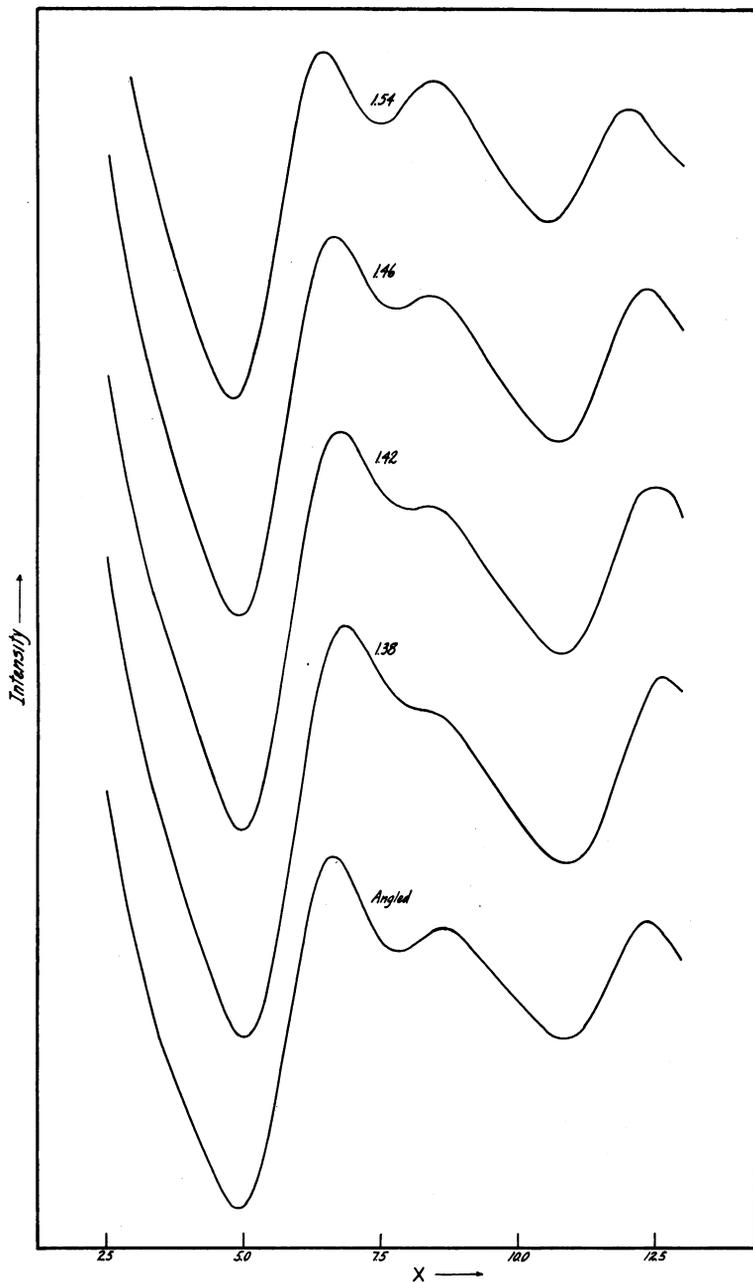
FIGURE 2

Theoretical intensity curves for diacetylene.

models. The a-values correspond to the carbon-nitrogen triple-bond distance for which 1.16 is the expected value.

Comparison with the standard CCl_4 photographs shows that no density correction is to be applied.

The lack of complete agreement among all of the a-values for a single model is expected on the basis of the St. John effect. I have found in working on electron-diffraction photographs that the measurement of an asymmetric ring (such as one of a pair of rings close together or one ring with a very different rate of decline in apparent density on the inside and outside) always gives a value for the interatomic distance which is different from that calculated from any sharp, well-defined ring. The discrepancy between the position of an asymmetric spectral line as measured subjectively with a filar micrometer and objectively by a recording microphotometer has been thoroughly investigated by St. John and Ware.[4] They show that the apparent maximum of such a line measured subjectively is always shifted toward the side of greater contrast, and the effect

TABLE 2

	$\dfrac{\text{SIN } \theta/2}{\lambda}$	1.46		1.42		1.38	
		x	a	x	a	x	a
1st min.	0.356	4.90	1.10	4.90	1.10	5.03	1.12
1st max.	0.430	6.63	1.23	6.70	1.24	6.80	1.26
2nd min.	0.753	10.75	1.14	10.80	1.14	10.90	1.15
2nd max.	0.833	12.32	1.18	12.53	1.20	12.65	1.21

on the measurement of a doublet is such that the apparent separation is greater than the true. The cause for this shift lies in the psychological effect of the difference in brightness of the background on the two sides of the line. A particularly clear example of this effect in the measurement of electron-diffraction photographs has been found in the case of sulphur hexafluoride; here the inner component of a double ring is shifted in by six per cent and the outer is shifted out by six per cent as determined by a comparison of the corresponding interatomic distances with those calculated from two sharp single rings lying farther out in the photograph. While the general appearance of the asymmetric characteristics of such a photograph is very useful in the qualitative comparison with theoretical curves, good quantitative agreement among all the rings is impossible. The exact size of the correction to be applied cannot be predicted, but an allowance for the effect may be made by determining the interatomic distance from the sharply defined single rings only.

The measurement of the position of the minima on the photograph also involves the St. John effect. This is particularly apparent in the first minimum because of the extreme density of the central image. Measurement of the photographs of fifteen different compounds taken with various

intensities shows that the position of the first minimum is always shifted out by from eight to ten per cent.

In table 1 for cyanogen the first minimum shows the usual deviation. The first maximum is of the type which shows the St. John effect and hence the corresponding a-value is larger than the correct one. The sharp second maximum affords a correct estimation of the value of a. The "1.38" model is not satisfactory, but the other two can scarcely be distinguished. The most probable values are chosen as follows:

$$C—N = 1.16 \pm 0.02 \text{ Å}$$
$$C—C = 1.43 \pm 0.03 \text{ Å}.$$
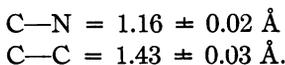
These results show that the single-bond models are somewhat more important than the double-bond models in the resonating structure which represents the structure of cyanogen.

The theoretical discussion for diacetylene is exactly the same as for cyanogen. The models calculated again vary from 1.54 to 1.38 for the central bond distance while the triple-bond distance is 1.22 and the carbon-hydrogen bond is 1.06 throughout. It will be noticed in figure 2 that the subsidiary maximum in the angled model is relatively less important than in the case of cyanogen.

The qualitative comparison as before eliminates the single-bond model; the quantitative comparison is indicated in table 2.

Comparison with the intensity standards indicates about a 1% correction. The values calculated from the sharp second maximum become 1.19, 1.21 and 1.22, respectively. The most probable values are

$$C—C \text{ at end} = 1.21 \pm 0.02 \text{ Å}$$
$$C—C \text{ in center} = 1.43 \pm 0.03 \text{ Å}.$$

TABLE 3
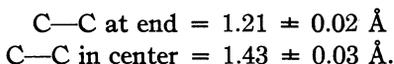
	$\dfrac{\text{SIN } \theta/2}{\lambda}$ OBSERVED	MODEL I 180°		MODEL II 150°		MODEL III 125°		MODEL IV 110°		MODEL V 90°		MODEL VI 50°	
		x	a	x	a	x	a	x	a	x	a	x	a
1st min.	0.282	4.72	1.335	4.75	1.343	4.60	1.300	4.35	1.230	4.25	1.201	4.63	1.309
1st max.	0.397	7.55	1.514	7.60	1.524	7.80	1.564	7.92	1.588	7.72	1.548	7.90	1.584
2nd min.	0.556	11.13	1.592	11.12	1.590	10.65	1.524	10.80	1.545	11.20	1.603	11.15	1.595
2nd max.	0.737	13.85	1.496	13.90	1.502	14.30	1.545	13.90	1.502	14.15	1.528	14.30	1.545
3rd min.	0.921	17.45	1.508	17.40	1.504	17.10	1.478	17.40	1.504	17.05	1.474	17.30	1.495
Mean value			1.528		1.530		1.528		1.535		1.538		1.555
Average deviation 0.033					0.030		0.027		0.032		0.037		0.035

Final value Cl—O = 1.53 ± 0.03 Å

This agrees satisfactorily with the result for cyanogen. The single bond model for diacetylene, too, makes a greater contribution to the final structure than that of the models containing only six bonding electron pairs.

I wish to express my appreciation to Professor Pauling at whose suggestion this investigation was undertaken, and to Dr. G. W. Wheland for the preparation of the diacetylene.

NOTE ON CHLORINE DIOXIDE

The experimental value for the chlorine-oxygen separation in ClO_2, which was published recently in these PROCEEDINGS,[5] is 0.05 Å too large because of a numerical error which occurred in the computation of the $\frac{\sin \theta/2}{\lambda}$ values from the observed ring diameters. Table 3 contains the corrected $\frac{\sin \theta/2}{\lambda}$ and a-values. The most probable value based upon this table is Cl—O = 1.53 ± 0.03 Å.

Although the combination of electron-pair with three-electron bond is surmised to produce a chlorine-oxygen separation of about 1.57 Å, which is midway between the single-bond and double-bond value, some deviation from this may well occur, and, inasmuch as it is impossible to write for ClO_2 any structure with double bonds which does not involve high-lying energy values, the observed separation of 1.53 Å can be explained only on the basis of the discussion previously given, so that this corrected result still substantiates the type of resonance represented by the three-electron bond. The separation in the combined bond is evidently nearer to that of the double-bond (1.48 Å) than to the single-bond distance (1.65 Å).

  * Contribution from Gates Chemical Laboratory, California Institute of Technology, No. 354.
  [1] Wierl, R., *Ann. Phys.*, 13, 453 (1932).
  [2] Pauling, Linus, these PROCEEDINGS, 18, 293 (1932).
  [3] Brockway, L. O., and Pauling, Linus, *Ibid.*, 19, 68 (1933).
  [4] St. John, C. E., and Ware, L. W., *Astrophys. Jour.*, 44, 35 (1916).
  [5] Brockway, L. O., these PROCEEDINGS, 19, 303 (1933).