has been studied from 50 to 275° and from 5 to 10 moles per liter, thus extending to high den-

sities, the data previously obtained.

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The Electron Diffraction Investigation of Methylacetylene, Dimethylacetylene, Dimethyldiacetylene, Methyl Cyanide, Diacetylene, and Cyanogen

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Introduction

In consequence of the apparent constancy and additivity of interatomic distances for covalently-bonded atoms[1] and of the dependence of interatomic distance on bond type, it has been found[2] that the determination of values of interatomic distances in molecules can be used in the study of the types of bonds represented in the molecules. This procedure is especially valuable in the study of conjugation and other resonance phenomena.[3] In order to test the postulate that the internuclear distance of two bonded atoms is determined essentially by the nature of the bond between the two atoms and is not at all or is only slightly influenced by the other bonds in the molecule an electron-diffraction investigation of isobutene, tetramethylethylene, mesitylene, and hexamethylbenzene was carried out[4]; this led to the conclusion that in these four molecules, in which there are methyl groups substituted in ethylene or benzene, the carbon–carbon single-bond distance has the same value, 1.54 ± 0.02 Å. (to within the estimated experimental error) as in other hydrocarbon molecules. Further support for this conclusion is provided by the recent X-ray investigation of crystalline hexamethylbenzene by Robertson and Brockway,[5] who have found 1.53 Å. for the bond distance for the methyl groups attached to the benzene ring, in place of the value 1.48 Å. reported some years ago.[6]

It is accordingly of great interest that the value found spectroscopically for the large moment of inertia of methylacetylene by Herzberg, Patat, and Verleger[7] and verified by Badger and Bauer[8] should lead, on the assumption that the other interatomic distances in the molecule have their normal values, to the value 1.462 ± 0.005 Å. for the carbon–carbon single-bond distance in this molecule, in which the single bond is adjacent to a triple bond. In order to evaluate this distance independently we have investigated methylacetylene by the electron-diffraction method, and have also investigated the related substances dimethylacetylene, dimethyldiacetylene, methyl cyanide, diacetylene, and cyanogen. The results of this work are described and discussed below.

Experimental Methods and Results

Preparation of Methylacetylene.—The attempt was first made to prepare methylacetylene by the method of Lebeau and Picon,[9] involving the action of methyl iodide on the sodium compound of acetylene in liquid ammonia solution. The yields were very small, however, and the method was abandoned. The substance was finally prepared by a modification of the method of Johnson and McEwen.[10] 1,2-Dibromopropane (55 g., b. p. 141° at 760 mm.), which was prepared for us by Professor H. J. Lucas, was run slowly into a solution of potassium hydroxide (56 g.) in 95% ethanol (56 ml.), heated in a reflux by an oil-bath at 160°. The gas evolved during the vigorous reaction was passed into a solution of cuprous chloride (prepared by the method of "Organic Syntheses," Coll. Vol. I, p. 163) in ammonium hydroxide (sp. gr. 0.880). The precipitated yellow copper derivative of methylacetylene was filtered off and suspended in water, an excess of concentrated hydrochloric acid was added, and the mixture was boiled under reflux. The evolved gas was dried in calcium chloride U-tubes at 0° and then collected as liquid in a tube cooled with solid carbon dioxide and isopropyl alcohol. The contamination of acetylene was removed by

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(2) L. Pauling, Proc. Nat. Acad. Sci., 18, 293 (1932); L. Pauling, L. O. Brockway and J. Y. Beach, THIS JOURNAL, 57, 2705 (1935).

(3) See, for example, a forthcoming paper by V. Schomaker and L. Pauling, to be published in THIS JOURNAL.

(4) L. Pauling and L. O. Brockway, ibid., 59, 1223 (1937).

(5) J. M. Robertson and L. O. Brockway, private communication.

(6) K. Lonsdale, Proc. Roy. Soc. (London), A123, 494 (1929).

(7) G. Herzberg, F. Patat and H. Verleger, J. Phys. Chem., 41, 123 (1937).

(8) R. M. Badger and S. H. Bauer, J. Chem. Phys., 5, 599 (1937).

(9) P. Lebeau and M. Picon, Compt. rend., 156, 1077 (1913).

(10) J. R. Johnson and W. L. McEwen, THIS JOURNAL, 48, 469 (1926).

fractional distillation, leaving methylacetylene, with b. p. −23° (760 mm.).

Dimethylacetylene.—The starting material for the preparation of dimethylacetylene was 2,3-dibromobutane (b. p. 158° at 760 mm.), prepared by Professor H. J. Lucas. This was converted into 2-bromo-2-butene by boiling with potassium acetate in glacial acetic acid.[11] This substance was then converted into dimethylacetylene by the method of Wislicenus and Schmidt,[12] involving heating to 180° with alcoholic potassium hydroxide in a closed tube. The tube was cooled to −20° before opening, and the contents

was added to copper methylacetylene (16 g.) suspended in water (500 ml.) and the mixture was distilled with steam. The resulting dimethyldiacetylene, which collects as a white solid, was recrystallized from ligroin; m. p. 64°.

Diacetylene.—The apparently simple method of Straus and Kollek[14] was tried several times, but was found to give very poor yields. Similar poor yields have been reported by Dr. G. W. Wheland.[15]

Small yields were obtained also by the very laborious method of Baeyer,[16] in which diacetylene dicarboxylic acid, $COOHC \equiv C - C \equiv CCOOH$, is prepared by the oxidation
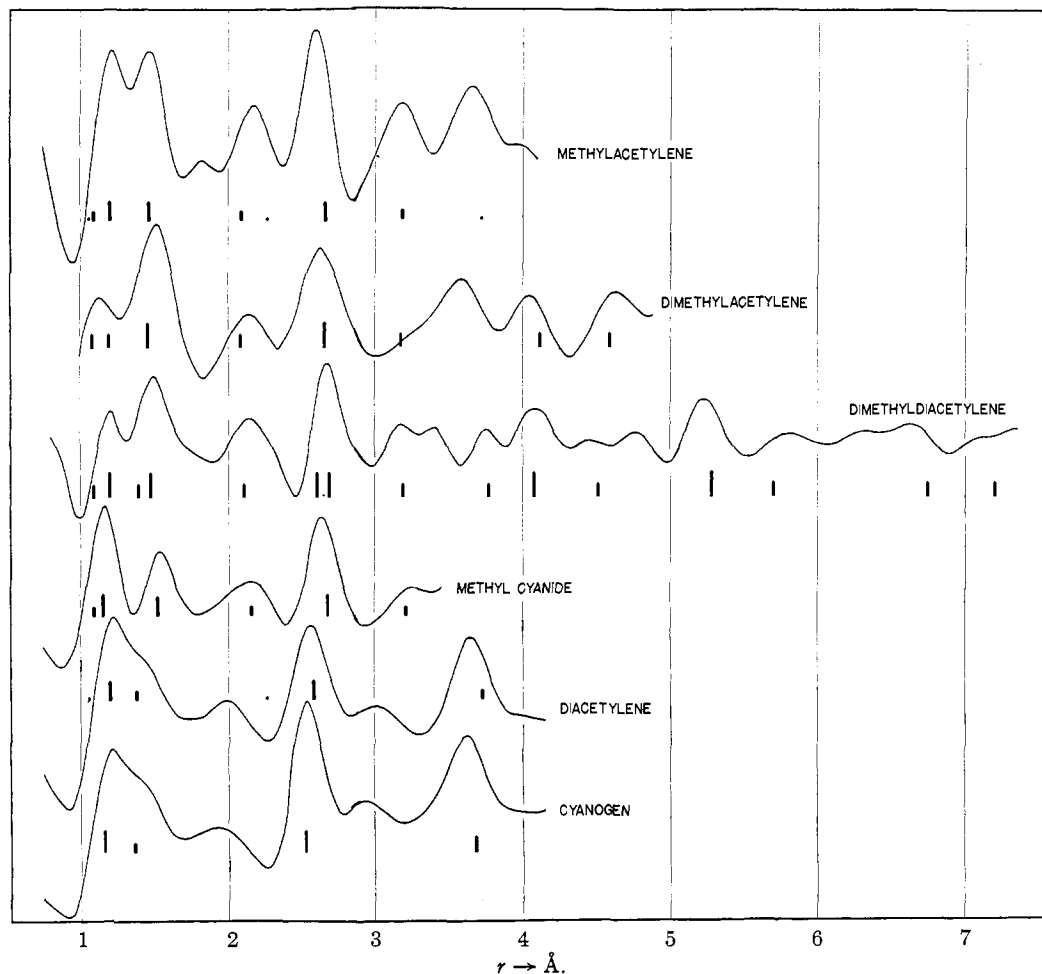

Fig. 1.—Radial distribution curves.

poured into ice-cold water. The acetylenic products were distilled into cold alcoholic silver nitrate solution, any precipitate filtered off, and the filtrate warmed to distil off the dimethylacetylene; b. p. 27° (760 mm.).

The compound was also prepared by the direct dehydrobromination of 2,3-dibromobutane by alcoholic potassium hydroxide.

Dimethyldiacetylene.—This substance was prepared by the method of Griner.[13] Potassium ferricyanide (90 g.)

of the copper derivative of propiolic acid by potassium ferricyanide and then decarboxylated by the reaction with cuprous chloride in liquid ammonia solution. This method would not have been used had not a supply of propiolic acid been available.

A satisfactory method, a modification of that of Griner[13] for dimethyldiacetylene, was finally developed. The copper derivative of acetylene (50 g.) suspended in water (500 ml.) was refluxed with potassium ferrocyanide (600

(11) E. G. Bainbridge, *J. Chem. Soc.*, **105**, 2291 (1914).

(12) J. Wislicenus and P. Schmidt, *Ann.*, **313**, 220 (1900).

(13) G. Griner, *Ann. chim. phys.*, [6] **26**, 354 (1892).

(14) F. Straus and L. Kollek, *Ber.*, **59**, 1664 (1926).

(15) Private communication.

(16) A. Baeyer, *Ber.*, **18**, 2273 (1885).

g.), and the evolved gas was dried over calcium chloride and collected in a U-tube cooled with solid carbon dioxide and isopropyl alcohol: m. p. −10°; b. p. 10° (760 mm.).

The Electron-Diffraction Technique.—In the preparation of the electron diffraction photographs of the gas molecules the apparatus constructed and described by Brockway[17] was used, with 10.85 cm. nozzle-to-film distance and 0.0613 Å. electron wave length, determined from photographs of gold foil. About ten photographs of each substance were prepared and measured.

Use was made in the interpretation of the photographs of the radial distribution method,[18] with coefficients obtained by multiplying the visually estimated intensity values by a factor such as se^{2-as^2}, as recommended by Schomaker and Degard,[19] as well as of the visual method of comparison with simplified calculated intensity curves.

The C–H distance for the methyl group was taken to be 1.09 Å. and that for acetylenic carbon 1.06 Å., and the bond angles in the methyl group were given the value 109°28′. All interatomic interactions except H–H were included in the intensity expressions.

Methylacetylene. — Excellent photographs, showing seven well-defined rings, were obtained of methylacetylene. The appearance of the photographs resembles closely that indicated by the calculated intensity curves of Fig. 2. In addition to the features for which s_0 and I values are given in Table I, a ring too faint to be measured could be seen between the sixth and seventh well-defined maxima, as indicated by the curves.

The radial distribution curve corresponding to the C values of Table I is shown in Fig. 1. Its three principal peaks, at 1.21, 1.47 and 2.60 Å., correspond to the three carbon–carbon distances, a, b, and $a + b$, in the molecule, $H_3C\overset{a}{-}C\overset{b}{\equiv}C-H$, and indicate the values 1.47 and 1.21 Å. for a and

b, respectively. The second of these is very close to the acetylene[20] value, 1.204 Å., and in the following analysis we shall assume that the triple-bond distance in the molecule is 1.20 Å., in order that the other carbon–carbon distance may be more precisely evaluated.

The intensity curves of Fig. 2 were calculated with $b = 1.20$ Å., C–H = 1.09 Å. for the methyl group and 1.06 Å. for the acetylenic hydrogen, and angles H–C–C = 109°28′ for the methyl group. It is seen that the quantitative compari-
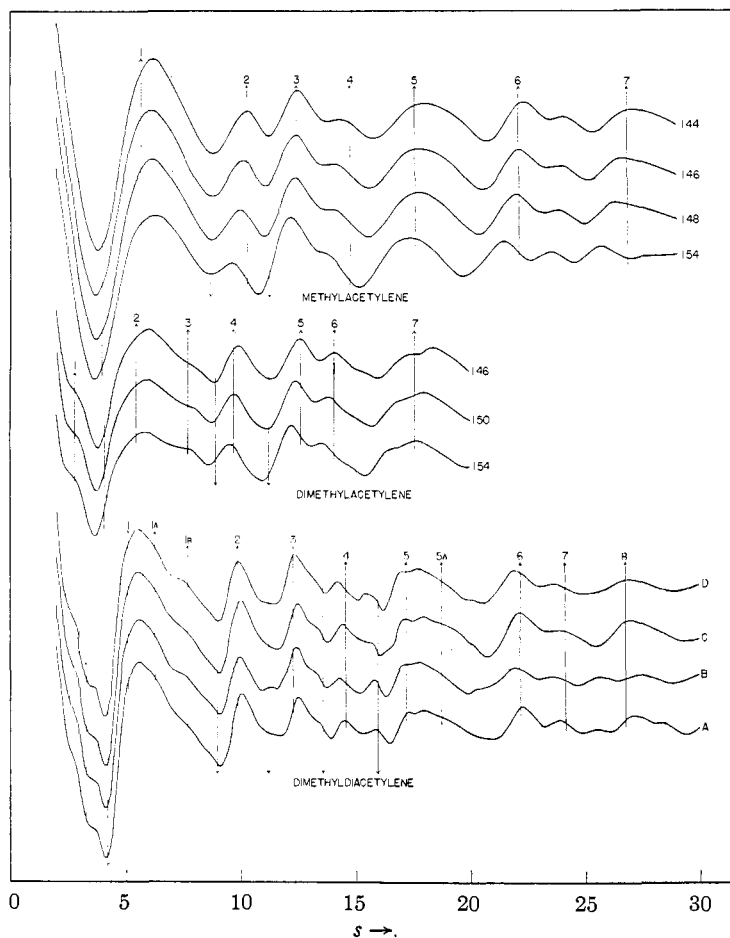

Fig. 2.—Calculated simplified intensity curves for methylacetylene, dimethylacetylene, and dimethyldiacetylene.

son with the observed values of s_0, indicated by vertical lines in the figure, is poor for the model with $a = 1.54$ Å. and good for the models with $a = 1.44$, 1.46, and 1.48 Å., with the 1.46 Å. model slightly more satisfactory than the other two. The average value of s/s_0 for this model, omitting the unreliable first minimum and first maximum

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

(18) L. Pauling and L. O. Brockway, THIS JOURNAL, **57**, 2684 (1935).

(19) Unpublished investigation.

(20) G. Herzberg, F. Patat and J. W. T. Spinks, *Z. Physik*, **91**, 386 (1934).

and the fourth maximum, which is represented as a shelf in the curve, is 0.998. We accordingly accept the value 1.46 ± 0.02 Å. for the distance a in methylacetylene as the result of the electron-diffraction investigation, with the value $b = 1.21 ± 0.03$ Å. given by the radial distribution curve. This result is in complete agreement with the spectroscopic value 1.462 ± 0.005 Å. mentioned in the introductory section of this paper.

TABLE I
METHYLACETYLENE

Max.	Min.	I	C	s_0	s^a	s/s_0
	1			4.01	3.73	(0.93)
1		10	6	5.71	6.13	(1.07)
	2			8.72	8.78	1.007
2		7	10	10.36	10.20	0.984
	3			11.30	11.18	.989
3		7	12	12.51	12.47	.997
	4			13.49	13.70	1.015
4		3	6	14.84	...	...
	5			15.99	15.65	0.979
5		5	9	17.67	17.83	1.009
6		3	4	22.13	22.18	1.002
7		1	1	26.87	26.76	0.996
					Average	.998
					C_1–C_2 =	1.457 Å.
					C_2–C_3 =	1.198 Å.

[a] Calculated for the model with C_1–C_2 = 1.46 Å., C_2–C_3 = 1.20 Å., C–H = 1.09 Å. (methyl group) or 1.06 Å., angle H–C–C = 109° 28' in methyl group.

Dimethylacetylene.—Photographs of dimethylacetylene were obtained showing seven rings, with the s_0 and I values given in Table II. The radial distribution curve (Fig. 1) has principal peaks at 1.50 and 2.63 Å. These indicate 1.50 and 1.43 Å., respectively, for the distance a in the molecule $CH_3 \overset{a}{—} C \overset{b}{\equiv} C \overset{a}{—} CH_3$, assuming 1.20 Å.

TABLE II
DIMETHYLACETYLENE

Max.	Min.	I	C	s_0	s^a	s/s_0
1		2	0	2.84	...	..
	2			4.13	3.70	(1.12)
2		10	8	5.50	5.90	(0.93)
3		2	3	7.73	...	..
	4			8.92	8.83	0.990
4		4	8	9.72	9.81	1.009
	5			11.28	11.28	1.000
5		6	12	12.68	12.50	0.986
6		2	4	14.10	14.00	.993
7		3	3	17.62	...	...
					Average	0.996
				C_1–C_2 = C_3–C_4 =	1.474 Å.	
				C_2–C_3 =	1.195 Å.	

[a] Calculated for the model with C_1–C_2 = C_3–C_4 = 1.48 Å., C_2–C_3 = 1.20 Å., C–H = 1.09 Å., and angles H–C–C = 109°28'.

the triple-bond separation b. The average of the two values is close to the value 1.46 Å. found in methylacetylene.

In Fig. 2 there are shown calculated intensity curves for three models, with a equal to 1.46, 1.50, and 1.54 Å., respectively; the other parameters have the values C–H = 1.09 Å., $b = 1.20$ A., and angle H–C–C = 109°28' for each model. The curves represent satisfactorily the appearance of the photographs, and their similarity is so great that a decision among them cannot be made from the qualitative comparison with the photographs. We again assume, however, that the C≡C distance has the triple-bond value 1.20 Å., and determine the value of the carbon–carbon distance to the methyl groups from the quantitative comparison of s and s_0 values. It is seen from the vertical lines in Fig. 2, representing the observed values s_0, that the best model lies between the 1.46 and the 1.50 model; the comparison in Table II is with the model with $a = 1.48$ Å., and leads to $a = 1.474$ Å. (The first and third rings are represented only as shelves in the curves. The second minimum, second maximum, and seventh maximum are not included in the average because of their unreliability.) We accordingly accept for this molecule the value $a = 1.47 ± 0.02$ Å., with b assumed to be 1.20 Å.

Dimethyldiacetylene.—The values of s_0 and I for the rings observed on the photographs of dimethyldiacetylene are given in Table III. The photographs have the general appearance suggested by the four curves shown in Fig. 2. Two rings very close to the central image, corresponding to the shelves at about $s = 2.7$ and 3.7 on the curves, could be seen but not accurately measured on the films. The first strong ring seemed to the eye to be composed of three maxima, as indicated in the table and by the vertical lines in the figure; this is apparently the result of an attempt to resolve the irregular contour of the intensity curve in this region into component symmetrical peaks.

The radial distribution curve calculated with the s_0 and C values of Table III is shown in Fig. 1. The first two peaks of the curve, at 1.20 and 1.49 Å., correspond to the distances b and a, respectively, in the molecule $CH_3 \overset{a}{—} C \overset{b}{\equiv} C \overset{c}{—} C \overset{b}{\equiv} C \overset{a}{—} CH_3$. Each of these distances occurs twice in the molecule, and has twice the weight of c, the peak for which is not resolved from that for b. The large peak at 2.67 Å. corresponds to $a + b$ and $b + c$,

unresolved. The next carbon–carbon peaks are at 3.76 Å. ($2b + c$) and 4.08 Å. ($a + b + c$); with the values given by the first peaks for b and a, these lead to 1.36 and 1.39 Å., respectively, for c. The values $a = 1.49$, $b = 1.20$, and $c = 1.38$ Å. are compatible with the two other carbon–carbon peaks, at 5.23 Å. ($a + 2b + c = 5.27$ Å.) and 6.64 Å. ($2a + 2b + c = 6.76$ Å.; one term only); and these values also lie very close to those for similar bonds in other molecules.

TABLE III

DIMETHYLDIACETYLENE

Max.	Min.	I	C	s_0	$s_C{}^a$	$s_A{}^b$	s_C/s_0	s_A/s_0
	1			4.22	4.15	4.15	0.983	0.983
1		10	2	5.09 ⎫	5.55	5.65	...	...
1a		2	1	6.25 ⎭				
1b		2	1	7.70	...	...	...	...
	2			8.97	9.06	9.12	1.010	1.017
2		6	6	9.87	10.03	10.09	1.016	1.022
	3			11.23	11.63	11.78	(1.04)	(1.05)
3		4	6	12.30	12.50	12.50	1.016	1.016
	4			13.56	13.80	13.95	1.018	(1.029)
4		2	3	14.60	14.47	14.53	0.991	0.995
	5			15.98	16.10	...	1.008	...
5		3	5	17.21	17.21	17.33	1.000	1.007
5a		1	2	18.78	...	...	...	...
6		2	4	22.19	22.19	22.30	1.000	1.005
7		1	2	24.18	24.05	23.95	0.995	0.990
8		1	1	26.79	27.00	27.22	1.008	1.016
						Average	1.004	1.006
					C_1–C_2 =	1.466 Å.	1.469 Å.
					C_2–C_3 =	1.205 Å.	1.207 Å.
					C_3–C_4 =	1.406 Å.	1.369 Å.

^{a} Calculated for the model (C) with C_1–C_2 = 1.46 Å., C_2–C_3 = 1.20 Å., and C_3–C_4 = 1.40 Å.

^{b} Calculated for the model (A) with C_1–C_2 = 1.46 Å., C_2–C_3 = 1.20 Å., and C_3–C_4 = 1.36 Å.

The four curves A, B, C, and D of Fig. 2 are calculated for models with the triple-bond distance b equal to 1.20 Å. and with the following values for a and c, respectively: A, 1.46, 1.36; B, 1.50, 1.36; C, 1.46, 1.40; and D, 1.50, 1.40 Å. The evidence supporting a choice among these models is small; however, model C is somewhat more satisfactory than the others, in that it alone of the four leads to a curve with no pronounced peak between the fourth and fifth rings, in which region no ring was visible on the photographs. Model B is rendered unsatisfactory by the facts that it leads to a curve showing a larger peak in this position than that for the observed fourth ring and showing no peak for the eighth ring. (All of the curves have a small peak between rings 5 and 5a. A slight indication of a subsidiary ring in this region could be seen on the photographs.)

The quantitative comparison of measured s_0 values and the calculated s values for models C and A is reported in Table III. Giving equal weights

to the values for the two models and the radial distribution curve, we find for the interatomic distances in dimethyldiacetylene the values $a = 1.47 \pm 0.02$ Å. (methyl-group single bond), $b = 1.20 \pm 0.02$ Å. (triple bond), and $c = 1.38 \pm 0.03$ Å. (central single bond).

Methyl Cyanide.—Good photographs of methyl cyanide were obtained, showing seven measurable rings. The s_0 values for these and for three apparent minima are given in Table IV, together with the estimated intensities of the rings and the values of C calculated from them.

TABLE IV

METHYL CYANIDE

Max.	Min.	I	C	s_0	s^a	s/s_0
	1			4.15	3.75	(0.90)
1		10	2	5.66	...	
2		6	2	7.54	...	
	3			8.96	9.08	1.013
3		4	2	10.09	10.15	1.006
	4			11.27	11.17	0.991
4		6	5	12.50	12.62	1.010
5		1	1	14.32	...	
6		4	3	17.42	17.93	(1.029)
7		2	1	22.20	22.30	1.005
					Average	1.005
					C–C =	1.487 Å.
					C–N =	1.156 Å.

^{a} Calculated for the model with C–C = 1.48 Å., C–N = 1.15 Å.

The radial distribution curve has peaks at 1.17, 1.53, 2.16, 2.63, and 3.25 Å. (Fig. 1), indicating that the carbon–carbon distance is only slightly smaller than the normal value 1.54 Å. In order to determine this distance more accurately by the comparison of the measured ring diameters with those given by calculated intensity curves the assumption may be made that the carbon–nitrogen distance has the triple-bond value 1.15 Å. The curves shown in Fig. 3 correspond to the values 1.54, 1.52, and 1.48 Å., respectively, for the carbon–carbon distance. The photographs are in approximate qualitative agreement with all of these curves. It may be pointed out that the first and second apparent maxima are not resolved in the calculated curves, and that the fifth apparent maximum seen on the photographs is represented in the curves by only a shelf. All three curves show a small deviation from the course indicated by the photographs in that the third ring, which appears to be nearly as strong as the fourth one, is represented by a much smaller peak.

It is seen from Fig. 3 that the quantitative comparison of the measured s_0 values with the positions of the peaks is more satisfactory for the 1.48 and 1.52 models than for the 1.54 model. In one qualitative aspect the 1.54 and 1.52 models are
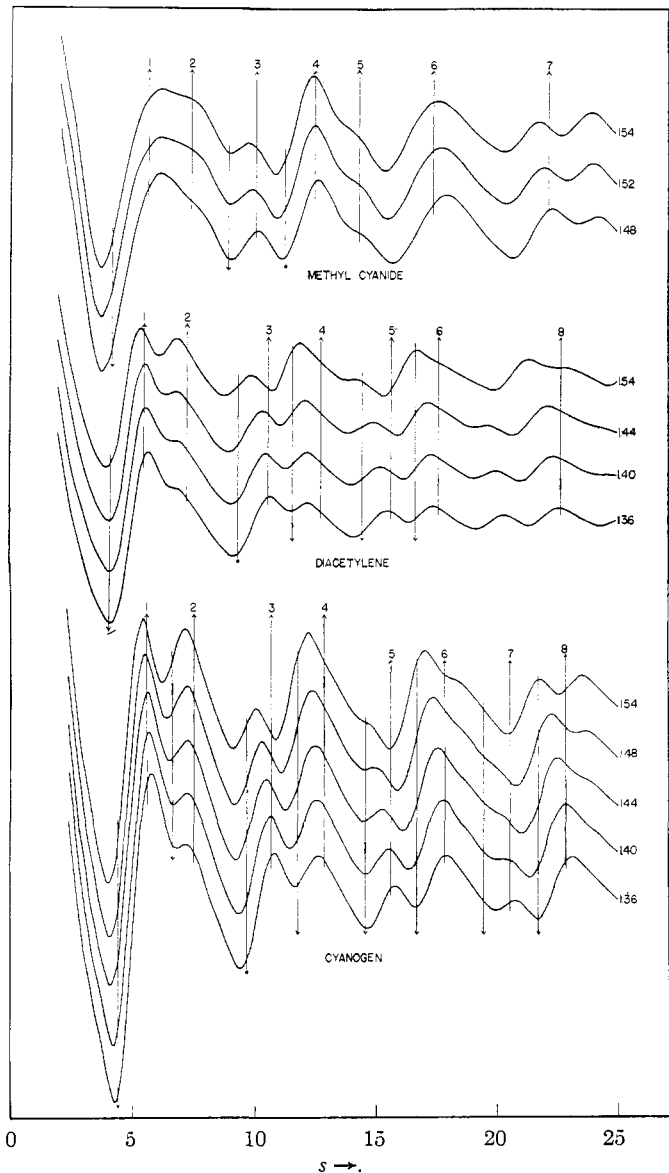

Fig. 3.—Calculated intensity curves for methyl cyanide, diacetylene, and cyanogen.

completely unsatisfactory: they show at $s \cong 24$ a peak which is larger than that at $s \cong 22$, whereas not a pronounced ring but only a very weak one can be seen just beyond the seventh ring on the photographs. (Another ring, which could not be measured reliably, can be seen at about $s_0 = 26$.) The 1.48 curve has only a small peak at $s \cong$

24, and is considered to be in satisfactory agreement with the photographs.

The comparison of s_0 values with the s values from this curve is given in Table III. The first, second, and fifth rings correspond to no definite values of s, and the first minimum, as usual, provides no reliable comparison. The sixth ring on the photographs appears to be followed by a shelf, and this asymmetry has probably caused the measured s_0 values to be low; hence the corresponding value of s/s_0 has been omitted in taking the average. The comparison leads to C–C = 1.49 Å. and C–N = 1.16 Å. It seems likely that these values are more reliable than those given by the radial distribution curve, in the calculation of which the less certain as well as the more certain s_0 values were involved. (The radial distribution peak at 2.63 Å. indicates 1.48 Å. for C–C, with C–N = 1.15 Å. assumed, whereas that at 1.53 Å. represents the C–C distance directly.) We accept as the result of the investigation of methyl cyanide the interatomic distances C–C = 1.49 ± 0.03 Å. and C–N = 1.16 ± 0.03 Å.

The carbon–carbon distance found is 0.05 Å. smaller than that reported by Brockway[21] in an earlier investigation carried out in these Laboratories. This difference is greater than that usually found in duplicate electron-diffraction investigations, and we have sought its source. At our request Dr. Verner Schomaker, who has shown especial skill in measuring electron-diffraction photographs, remeasured five of the older films made by Brockway and four of our newer ones, without knowledge of the results of our measurements. He reported the two sets of photographs to be identical in appearance, except in intensity, and he found all of the features which we had observed. (In addition he measured an inner ring at $s_0 = 1.81$, which is represented only by an inflection on the calculated curves, and the sixth minimum, which was also measured by Brockway but not by us.) His s_0 values are compared with Brockway's and ours in the following table.

It is seen that Schomaker's measurements of both the older and the newer films agree closely with ours, but that Brockway's s_0 values are low by an average of 1.3%. Brockway also included the unreliable broad sixth ring in his average, and used the 1.54 model for comparison, his films not showing the features near $s_0 = 24$ by means of which we eliminated this model. These differences combined to lead him to the larger C–C value 1.54 Å.

(21) L. O. Brockway, THIS JOURNAL, 58, 2516 (1936).

MEASURED VALUES OF s_0 FOR METHYL CYANIDE

Max.	Min.	Older films		Newer films P., S., and P.	
		L. O. B.	V. S.		V. S.
	1		3.88	4.15	3.96
1		7.19	⎰ 5.69	5.66	5.71
2			⎱ 7.56	7.54	7.71
	3	8.60	8.89	8.96	8.96
3		9.84	10.05	10.09	10.03
	4	11.17	11.27	11.27	11.27
4		12.44	12.46	12.50	12.48
5		14.53	14.53	14.32	14.67
	6	15.75	15.91	...	15.95
6		17.16	17.46	17.42	17.23
7		21.77		22.20	22.12

Diacetylene.—On the photographs of diacetylene there are eight rings, of which the first six occur in pairs, as indicated by the calculated intensity curves 1.36 and 1.40 of Fig. 3, which reproduce the appearance of the photographs satisfactorily. Values of s_0 for seven of these maxima (the seventh ring was too faint to be measured) and for five minima are given in Table V.

TABLE V

DIACETYLENE

Max.	Min.	I	C	s_0	s^a	s/s_0
1		6	8	5.55	5.65	0.983
2		3	5	7.33		
	3			9.39	9.15	.975
3		4	10	10.64	10.64	1.000
	4			11.64	11.42	0.979
4		3	8	12.74	12.23	.961
	5			14.54	14.08	.969
5		1	3	15.70	15.40	.981
	6			16.72	16.32	.976
6		2	4	17.69	17.39	.978
8		1	2	22.70	22.52	.993
				Average		0.981
				C_2-C_3 =		1.364 Å.
				C_1-C_2 = C_3-C_4 =		1.187 Å.

^{a} Calculated for the linear model with C_1-C_2 = C_3-C_4 = 1.20 Å., C_2-C_3 = 1.38 Å., C–H = 1.06 Å.

The 1,2 and 3,4 carbon–carbon distances can be assigned the value 1.20 Å., as in acetylene. This value is given approximately (1.22 Å.) by the first peak of the radial distribution curve (Fig. 1); the slightly high value is probably due to incomplete resolution of the 2,3 peak, which appears as a shelf at about 1.40 Å. The next strong peak is at 2.56 Å., indicating 1.36 Å. for the 2,3-distance.

The intensity curves of Fig. 3 are calculated with C–C = 1.20 Å. for the 1,2- and 3,4-bonds and 1.54, 1.44, 1.40, and 1.36 Å., respectively, for the 2,3 bond. The 1.54 and 1.44 curves are eliminated by the observed intensity ratio 8:6 for

the third and fourth rings, this ratio being given best by the 1.36 curve. The intensity ratio 2:4 for the fifth and sixth rings, on the other hand, is not shown by the 1.36 curve, whereas the 1.40 curve reproduces this ratio satisfactorily. We accordingly accept an intermediate configuration of the molecule, with the ratio of distances C_2-C_3/C_1-C_2 = 1.38/1.20, as indicated by the qualitative analysis of the photographs.

The quantitative comparison of s_0 and s for this configuration (Table V) leads to the average value s/s_0 = 0.981. We accordingly assign to the interatomic distances in the molecule the values C_1-C_2 = C_3-C_4 = 1.19 ± 0.02 Å. and C_2-C_3 = 1.36 ± 0.03 Å.

TABLE VI

CYANOGEN

Max.	Min.	I	C	s_0	s^a	s/s_0
1		10	8	5.60	5.80	(1.035)
	2			6.65	6.88	(1.034)
2		4	5	7.53	7.23	(0.960)
	3			9.69	9.46	(0.976)
3		6	10	10.69	10.86	1.015
	4			11.82	11.70	0.990
4		4	8	12.91	12.70	0.984
	5			14.62	14.70	1.006
5		2	5	15.65	15.85	1.013
	6			16.72	16.68	0.998
6		3	6	17.86	17.95	1.005
7		1	1	20.57	20.78	1.010
8		2	2	22.83	23.11	1.012
				Average		1.004
				C–N =		1.155 Å.
				C–C =		1.366 Å.

^{a} Calculated for the linear model with C–N = 1.15 Å. and C–C = 1.36 Å.

Cyanogen.—The photographs of cyanogen are similar in appearance to those of diacetylene (Table VI). In Fig. 3 there are shown intensity curves calculated for linear models N≡C—C≡N with C–N = 1.15 Å. (the triple-bond value) and C–C = 1.54, 1.48, 1.44, 1.40, and 1.36 Å., respectively. Of these only the 1.40 and 1.36 curves reproduce the appearance of the photographs at all satisfactorily. The sequence of intensities and the relative positions of rings are reproduced almost perfectly by the 1.36 curve.

The quantitative comparison of s and s_0 leads to the average value s/s_0 = 1.004 (the first four values being not included in the average), corresponding to C–N = 1.16 ± 0.02 Å., and C–C = 1.37 ± 0.02 Å. The radial distribution curve (Fig. 1), with principal peaks at 1.22 and 2.53 Å., is compatible with these dimensions.

TABLE VII

INTERATOMIC DISTANCES

		Carbon–carbon distances, Å.			Carbon–nitrogen triple-bond distance, Å.
Molecule		Single bond adjacent to triple bond	Triple bond	Single bond between two triple bonds	
Methylacetylene	$CH_3C \equiv CH$	1.46 ± 0.02	1.20 ± 0.03		
Dimethylacetylene	$CH_3C \equiv CCH_3$	1.47 ± 0.02	(1.20)[a]		
Dimethyldiacetylene	$CH_3C \equiv C—C \equiv CCH_3$	1.47 ± 0.02	1.20 ± 0.02	1.38 ± 0.03	
Diacetylene	$HC \equiv C—C \equiv CH$		1.19 ± 0.03	1.36 ± 0.03	
Cyanogen	$N \equiv C—C \equiv N$			1.37 ± 0.02	1.16 ± 0.02
Methyl cyanide	$CH_3C \equiv N$	1.49 ± 0.03			1.16 ± 0.03

[a] Value assumed in the structure determination.

Discussion

The values of interatomic distances found for the molecules of the substances studied are given in Table VII. Of the six substances, three have been investigated previously by the electron-diffraction method. A study of diacetylene and cyanogen was made by Brockway[22] five years ago, when the technique of the method had not yet been brought to its present state. Brockway's photographs, with rings visible to $s = 13$, were interpreted to lead to the normal triple-bond distances and to the value 1.43 Å. for the central single-bond distance for both substances. In the present investigation photographs much superior to the earlier ones were obtained, showing rings out to $s = 23$. There is little reason to question the reliability of the new values 1.36 ± 0.03 Å. and 1.37 ± 0.02 Å. for the central single-bond distance in diacetylene and cyanogen, respectively.

An earlier investigation of methyl cyanide by Brockway[21] has been discussed above.

The carbon–carbon single-bond distance in methylacetylene is found to be 1.46 ± 0.02 Å. This result substantiates the value 1.462 ± 0.005 Å. reported from spectroscopic data,[7,8] and leaves no doubt that in this substance the interatomic distance for a carbon–carbon single bond adjacent to a carbon–carbon triple bond is less by about 0.08 Å. than the normal value 1.54 Å.

This shortening is shown to be characteristic for a carbon–carbon single bond adjacent to a carbon–carbon triple bond by the fact that the value 1.47 ± 0.02 Å. found for both dimethylacetylene and dimethyldiacetylene is the same to within the probable error as that for methylacetylene.

The shortening phenomenon is of great interest with respect to the use of interatomic-distance values in the discussion of resonance of the types

which give partial double-bond character to bonds in conjugated systems, and it is desirable to summarize the observations relevant to the phenomenon and to search for a suitable interpretation of them.

The pertinent observations are the following:

1. The carbon–carbon single-bond distance in methylacetylene is 0.08 Å. less than the normal value.

2. Approximately the same shortening (0.07 ± 0.02 Å.) is observed in dimethylacetylene, in which two carbon–carbon single bonds are adjacent to the triple bond, and in dimethyldiacetylene.

3. The carbon–carbon single bond adjacent to the carbon–nitrogen triple bond in methyl cyanide seems to be shortened by a somewhat smaller amount, 0.05 ± 0.03 Å.

4. The carbon–carbon single-bond distance has its normal value in tetramethylethylene, hexamethylbenzene, and related compounds,[4] in which it is adjacent to a double bond or benzene ring.

5. The carbon–hydrogen bond distance is less for acetylene (1.057 Å.) and hydrogen cyanide (1.057 Å.)[23] than for methane (1.093 Å.).[24] The value 1.087 Å. for ethylene and allene, calculated by Eyster[25] from the bond stretching force constants by use of a variant of Badger's rule,[26] is close to that for methane.

The Carbon–Hydrogen Bond Distance.— There are two reasonable ways of accounting for the observed shortening of single bonds adjacent to triple bonds: first, as the result of a change in the single-bond covalent radius of a triple-bonded carbon atom from the normal value; and, second,

(22) L. O. Brockway, Proc. Natl. Acad. Sci., 19, 868 (1933).

(23) G. Herzberg, F. Patat and Y. Verleger, Z. Physik, 102, 1 (1936); P. F. Bartunek and E. F. Barker, Phys. Rev., 48, 516 (1935).

(24) R. G. Dickinson, R. T. Dillon and F. Rasetti, ibid., 34, 582 (1929); N. Ginsburg and E. F. Barker, J. Chem. Phys., 3, 668 (1935).

(25) E. H. Eyster, ibid., 6, 580 (1938).

(26) R. M. Badger, ibid., 2, 128 (1934).

as the result of a change in bond type of the single bond (assumption of partial double-bond character).

The first of these must be accepted for carbon–hydrogen bond shortening. The hydrogen atom has only one stable orbital ($1s$), which can be used for formation of a covalent bond (with the normal amount of ionic character[27]); it is not possible for a molecule to show resonance with a structure involving a double bond to a hydrogen atom. Moreover. experience indicates that a small change in the amount of ionic character of a single bond does not cause an appreciable change in the bond distance. We are consequently led to attribute the decrease in the carbon–hydrogen bond length from 1.093 Å. in methane to 1.057 Å. in acetylene and hydrogen cyanide to differences in the single-bond covalent radii of the two atoms in these different molecules.

A decreased single-bond covalent radius for a carbon atom forming a triple bond may well be ascribed to increase in the value of the s coefficient of the hybrid $s - p$ bond orbital above the normal value $1/2$ for a tetrahedral bond orbital.[28] If the s orbital were divided equally between the single-bond orbital and the cylindrically-symmetrical orbital of the triple bond, its coefficient would be $1/2^{\frac{1}{2}}$ for each; it is probable, however, that because of the small triple-bond interatomic distance the triple-bond orbital involves a somewhat larger amount of the s orbital, and that the s coefficient for the single-bond orbital is increased only part way from 0.500 to the limit 0.707.

For a single-bond orbital of a carbon atom forming a double bond, as in ethylene, allene, or benzene, the s coefficient is expected to increase from $1/2$ toward the limiting value $1/3^{\frac{1}{2}} = 0.577$. We accordingly conclude, in agreement with observation, that a double bond or aromatic nucleus is much less effective than a triple bond in changing the properties of an adjacent carbon–hydrogen bond.

It is found empirically[29] that bonds involving hydrogen atoms are more variable in length and show greater deviations from additivity of equilibrium distances than other single bonds. We would hence expect that the carbon–carbon single-bond distance in methylacetylene and related substances would be less than the normal value 1.54

(27) L. Pauling, THIS JOURNAL, **54**, 3570 (1932).
(28) L. Pauling, *ibid.*, **53**, 1367 (1931).
(29) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, **1939**, Sec. 21.

Å. by an amount somewhat smaller than 0.036 Å. (the observed C–H shortening), perhaps by about 0.02 Å., and that the effect of an adjacent double bond or aromatic nucleus would be smaller still, probably less than 0.01 Å. These expectations are in agreement with the experimental results for the methylethylenes and methylbenzenes.
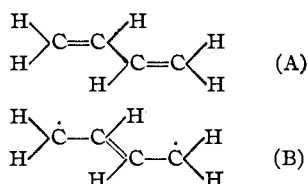
Resonance in Methylacetylene and Related Substances.—It seems probable that the large decrease of 0.07 or 0.08 Å. below the normal single-bond value observed for the methylacetylenes is to be explained in the main in the second way mentioned above, as resulting from partial double-bond character given the bonds by the contribution of unconventional electronic structures to the normal states of the molecules. The conventional structure (A) for methylacetylene, for example

is somewhat more stable than the structures B, C, and D, which contain one less covalent bond than A. These less stable structures would, however, be expected to make some contribution to the normal state of the molecule, and thus to give the C_1–C_2 bond some double-bond character, leading to decrease in the bond length.[2,4]

Resonance of this type does not occur for acetylene itself, because of the fact that the fourth orbital of carbon is not suited to the formation of a bond in the direction of the triple bond,[28] and a quadruple bond is hence not stable.
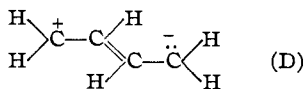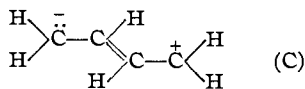
The postulated methylacetylene resonance is closely related to the resonance occurring in conjugated systems. Thus we attribute to the central bond in butadiene some double-bond character because of resonance between the conventional structure A and less stable structures such as B, C, and D

(C)

(D)

The analogy with methylacetylene is seen to be very close. The most striking aspect of the methylacetylene resonance is that it involves the rupture of a single bond (the bond to hydrogen), whereas in ordinary conjugated systems the corresponding change is that from a double bond to a single bond. Resonance of a closely similar type to that in the methylacetylenes has been postulated by Wheland[30] in explanation of the effect of alkyl groups in stabilizing hydrocarbon free radicals.

If we accept this interpretation of the shortening in methylacetylene, the observed effect can be interpreted with use of the empirical function relating bond distance and amount of double-bond character,[4] leading to the conclusion that the total contribution of structures such as B, C, and D to the normal state of the molecule is 18%. (If it be assumed that the change in covalent radius leads to an effect of 0.02 Å. and double-bond character to the remaining 0.06 Å., the indicated contribution of these structures is about 12%.) Since each of the three hydrogen atoms of the methyl group can enter into this conjugation with the triple bond, the contribution per hydrogen atom is between 4 and 6%.

In dimethylacetylene the two methyl groups compete to some extent for the triple bond, and in consequence the effect of conjugation should be somewhat less than for methylacetylene. The decrease reported, 0.07 Å., differs from that for methylacetylene, 0.08 Å., in the direction and by about the amount expected, but this cannot be considered significant because of the magnitude of the probable errors of the values.

The reason for a difference between the carbon–carbon bond distance in methyl cyanide and that in the methylacetylenes is not obvious. The greater electronegativity of nitrogen than of carbon should cause structures such as C to be unimportant, but should also enhance the contribution of structures such as D.

Our interpretation of the shortening in methyl cyanide and the methylacetylenes as due mainly to partial double-bond character provides justi-

fication for the interpretation of observed interatomic distances in metal carbonyl[31] and metal cyanide[32] molecules and complex ions in terms of partial double-bond character of the M–C bonds.

Whereas a triple bond, with effective cylindrical symmetry resulting from its two p bonds, can conjugate with all three C–H bonds of a methyl group, a double bond is expected to conjugate only with bonds lying in the $\overset{C}{\diagdown}_{C=C}$ plane. In the methylethylenes and methylbenzenes, with only one of the three carbon–hydrogen bonds of each methyl group lying approximately in this plane, the expected amount of double-bond character for a CH_3–C bond is 4 to 6 per cent., corresponding to 0.03 Å. decrease in bond length. Although the value 1.51 Å. for the bond distance. is not rigorously eliminated by the electron–diffraction and X-ray measurements on the methylethylenes and methylbenzenes,[4,5] the average experimental value is 1.53 Å., and it seems likely that the amount of conjugation of a methyl group with a double bond or benzene ring is less than one-third as great as that with the carbon–carbon triple bond.

Resonance in Conjugated Systems.[33]—There is now available sufficient information to permit a preliminary survey to be made of the amounts of double-bond character assumed by the bonds conventionally represented as single bonds in conjugated systems, as indicated by the observed values of the corresponding interatomic distances.

The six types of conjugated systems involving double bonds, aromatic nuclei, and triple bonds are shown in Table VIII, together with the observed interatomic distance values for those substances which have been investigated with some care. (No thoroughly reliable study has been made of a molecule representing the type
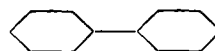
the values reported for biphenyl and p-diphenylbenzene are less certain than the other values in the table.) The shortening below the normal bond distance 1.54 Å. can be interpreted directly with use of the empirical curve[2,4] for the first three

(30) G. W. Wheland, *J. Chem. Phys.*, **2**, 474 (1934).

(31) L. O. Brockway and P. C. Cross, *J. Chem. Phys.*, **3**, 828 (1935); L. O. Brockway, R. V. G. Ewens and M. W. Lister, *Trans. Faraday Soc.*, **34**, 1350 (1938).

(32) L. Pauling, ref. 29, Sec. 31b.

(33) See also in this connection J. E. Lennard-Jones, *Proc. Roy. Soc.* (London), **A158**, 280 (1937); J. E. Lennard-Jones and J. Turkevich, *ibid.*, **A158**, 297 (1937); W. G. Penney, *ibid.*, **A158**, 306 (1937); W. G. Penney and G. J. Kynch, *ibid.*, **A164**, 409 (1938); J. M. Robertson, *J. Chem. Soc.*, 131 (1938).

TABLE VIII

INTERATOMIC DISTANCES FOR SINGLE BONDS IN CONJUGATED SYSTEMS

Type of conjugated system	Substance	Observed C–C distance,[h] Å.	Reference	Amount of double-bond character, %
	Butadiene	1.46 ± 0.03	a	18 ± 10
	Cyclopentadiene	1.46 ± .03	a	18 ± 10
	Stilbene	1.44 ± .02	b	25 ± 7
	p-Diphenylbenzene	1.46 ± .04	c	18 ± 12
	Biphenyl	1.48 ± .04	d	13 ± 12
	Vinylacetylene		e	
	Tolane	1.40 ± .02	f	33 ± 8
	Diacetylene	1.36 ± .03	g	44 ± 13
	Cyanogen	1.37 ± .02	g	38 ± 10
	Dimethyldiacetylene	1.38 ± .03	g	34 ± 13

[a] V. Schomaker and L. Pauling, ref. 3. [b] J. M. Robertson and I. Woodward, *Proc. Roy. Soc.* (London), **A162**, 586 (1937). [c] L. W. Pickett, *ibid.*, **A142**, 333 (1933); "Strukturbericht," Vol. III, pp. 682, 781. [d] J. Dhar, *Indian J. Phys.*, **7**, 43 (1932). [e] The electron-diffraction study of vinylacetylene and divinylacetylene is being carried out by Dr. V. Schomaker. [f] J. M. Robertson and I. Woodward, *Proc. Roy. Soc.* (London), **A164**, 436 (1938). [g] This investigation. [h] The values for probable errors are those of the original investigators, when given, or those estimated by us.

types of conjugated systems to give the amounts of double-bond character listed in the last column of the table. For the other systems involving one or two triple bonds, a correction of 0.02 Å. is made for each triple bond, for the reason indicated in the preceding section.

A bond between two double bonds, two benzene rings, or a double bond and a benzene ring is seen to have about 20 or 25% double-bond character, with no pronounced difference in conjugating power of a double bond and a benzene ring indicated. This is in accordance with the theoretical result reported five years ago,[34] that the conjugating power of a benzene ring differs from that of a double bond by only a small amount (about 10%, that of the double bond being the greater).

Since only the p_z orbitals of a triple bond are involved in conjugation with a double bond or benzene ring, the same conjugating power is expected for a triple bond as for a double bond; the experimental result for tolane, however, indicates a somewhat larger amount of double-bond character (about 30%) than for the first three systems. It is possible that conjugation is more complete for a system involving one triple bond than for the first three systems because of the absence of the effect of rotational oscillation, which inhibits resonance somewhat by bringing the molecules into non-coplanar configurations.

Two conjugated triple bonds can interact through either their p_z orbitals or their p_y orbitals

(34) L. Pauling and J. Sherman, *J. Chem. Phys.*, **1**, 679 (1933).

(taking the x axis along the line of the nuclei), so that we expect twice as great conjugation for this system as for two conjugated double bonds. This is verified experimentally, the amount of double-bond character found for diacetylene, dimethyldiacetylene, and cyanogen being about 40%.

We express our thanks to Professor H. J. Lucas for giving us starting materials for the preparation of the methylacetylenes, to Dr. S. Weinbaum for assistance with the calculations, and to Dr. V. Schomaker for remeasuring the photographs of methyl cyanide.

Summary

The electron-diffraction study of gas molecules of methylacetylene, dimethylacetylene, dimethyldiacetylene, methyl cyanide, diacetylene, and cyanogen has been carried out, leading to the interatomic distances given in Table VII.

It is suggested that the decrease below the normal value 1.54 Å. for a single bond adjacent to a triple bond found for the methylacetylenes (1.46–1.47 Å.) and methyl cyanide (1.49 Å.) is due partly to a change in single-bond radii (by about 0.02 Å.) and mainly to the assumption of partial double-bond character by the single bond.

The values found for a single bond between two conjugated triple bonds (1.36–1.38 Å. in diacetylene, dimethyldiacetylene, and cyanogen) are interpreted as indicating about 40% double-bond character for this bond, the amount of conjugation being about twice that for systems involving double bonds and benzene rings.