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Carbon–Carbon Bond Distances. The Electron Diffraction Investigation of Ethane, Propane, Isobutane, Neopentane, Cyclopropane, Cyclopentane, Cyclohexane, Allene, Ethylene, Isobutene, Tetramethylethylene, Mesitylene, and Hexamethylbenzene. Revised Values of Covalent Radii

BY LINUS PAULING AND L. O. BROCKWAY

In our studies of the dependence of interatomic distances on resonance[1] we have assumed that the carbon–carbon single bond is characterized by the distance 1.54 Å. (as in diamond) and we have attributed shortening of bond distances below 1.54 Å., such as is observed for the central bond in cyanogen,[2] diacetylene,[2] biphenyl,[3] and other conjugated systems, to partial double-bond character resulting from resonance. Some question has been raised as to whether or not this interpretation is justified, on the basis that the single-bond radius for aromatic carbon might be different from that for aliphatic carbon, as is indicated by the X-ray work of Mrs. Lonsdale on hexamethylbenzene.[4] In order to obtain information about this and to investigate also the constancy of carbon–carbon bond distances in non-resonating molecules we have during the past three years determined the configurations of thirteen hydrocarbons by the electron diffraction method; the results of this investigation are reported below.

In the course of the work it was found that the value assumed five years ago for the carbon double-bond covalent radius (obtained by linear interpolation between the single-bond and the triple-bond radius) is 0.02 Å. too large; in consequence of this we have been led to revise the double-bond radii of other atoms also.

Ethane, Propane, Isobutane, and Neopentane.—The samples of ethane, propane, and isobutane used were provided by Dr. B. H. Sage of these Laboratories, and that of neopentane by Dean F. C. Whitmore, from a preparation made by Mr. G. H. Fleming at Pennsylvania State College. Electron diffraction photographs, showing six to eight rings, were prepared by the usual method,[5] the distance from the gas nozzle to film being about 10 cm. and the electron wave length about 0.06 Å. Values of $s_0 = (4\pi \sin \theta/2)/\lambda$ for the apparent maxima and minima, obtained by averaging the measurements on about ten films for each substance, are given in Tables I to IV, together with visually estimated values of the intensities of the rings for use in application of the radial distribution method.[6]

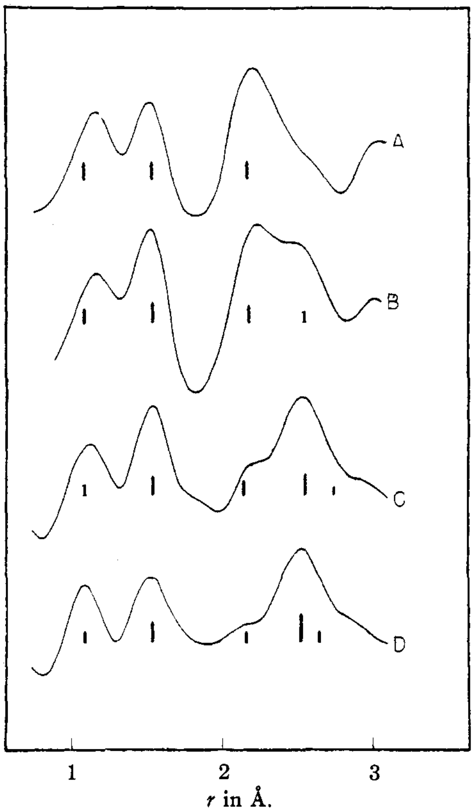

Fig. 1.—Radial distribution curves for (A) ethane, (B) propane, (C) isobutane and (D) neopentane. The positions of the heavy arrows indicate the interatomic distances determined by the comparison of the photographs with theoretical intensity curves; their heights show the relative scattering power associated with each distance.

The six-term radial distribution function for ethane (Fig. 1, curve A) shows maxima at 1.16,

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[1] (a) L. Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293 (1932); (b) L. Pauling, L. O. Brockway, and J. Y. Beach, THIS JOURNAL, **57**, 2705 (1935).

[2] L. O. Brockway, *Proc. Nat. Acad. Sci.*, **19**, 868 (1933).

[3] J. Dhar, *Indian J. Phys.*, **7**, 43 (1932).

[4] K. Lonsdale, *Proc. Roy. Soc.* (London), **A123**, 494 (1929).

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

[6] L. Pauling and L. O. Brockway, THIS JOURNAL, **57**, 2684 (1935).

1.52, and 2.21 Å. With consideration of the incomplete resolution of the first two maxima, this indicates that the C–C bond distance is somewhat greater than 1.52 Å. and the C–H bond distance somewhat less than 1.16 Å. Intensity curves calculated for (A) C–H = 1.06 Å., C–C = 1.54 Å., (B) C–H = 1.09 Å., C–C = 1.54 Å., and (C) C–H = 1.12 Å., C–C = 1.54 Å., with all angles given the tetrahedral value 109°28′, are represented in Fig. 2, the *trans* configuration of methyl groups indicated by recent thermochemical studies[7] being assumed in evaluating the H–H separations, which make only a small contribution. The curves do not differ greatly in qualitative aspect; the intensities of the three strong rings on the photographs, however, indicate that model B is somewhat better than either of the others. The quantitative comparison for this model, given in Table I, leads to the final values C–C = 1.55 ± 0.03 Å. and C–H = 1.09 ± 0.03 Å., in approximate agreement with the value C–C = 1.52 ± 0.10 Å. (with C–H = 1.10 Å. assumed) obtained by Wierl[8] by measurement of the three strong rings appearing on his photographs.

In ethane it was possible to consider the C–H distance as a parameter and to evaluate it as 1.09 ± 0.03 Å. In the case of the other hydrocarbons studied in this investigation (aside from ethylene) there are so many structural parameters that the experimental evaluation of the C–H distance cannot be carried out conveniently. We have accordingly assumed values for this distance in these substances, namely, C–H = 1.09 Å. for a carbon atom which forms four single bonds to other atoms (as in a methyl group) and C–H = 1.06 Å. for a carbon atom which forms a double bond. There is very little doubt that these values are correct to within about 0.03 Å., and in no case would a change of 0.03 Å. in the assumed C–H values change the values given in our investigation for the other interatomic distances by as much as 0.01 Å. The reasons for our choice of C–H values are the following. The table of covalent radii gives the value C–H = 1.06 Å., with use of the hydrogen radius provided by the hydrogen halides. This value is found experimentally to be valid for a carbon atom which forms a triple bond, 1.057 Å. being reported for both acetylene and hydrogen cyanide.[9] The value 1.06 ± 0.03 Å. for carbon forming a double bond is given by our study of ethylene, described later in this paper. On the other hand, the somewhat larger value 1.09 Å. which we have reported for ethane is supported by the spectroscopic values 1.08 and 1.093 Å. for methane.[10]

TABLE I

ETHANE

Max.	Min.	I	s_0	s^a	C–C. Å.
1		1	3.50		
2		6	6.15	6.40	(1.60)[b]
	3		7.51	7.81	(1.60)
3		5	9.07	9.00	1.528
	4		10.80	10.83	1.545
4		4	12.59	12.76	1.561
5		3	17.60	18.07	1.581
6		2	21.52	21.27	1.522
				Average	1.547 Å.

[a] Calculated for the model with C–H = 1.09 Å., C–C = 1.54 Å. and the angle H–C–H = 109°28′.

[b] In this table and the following ones the less reliable values, not included in taking the average, are shown in parentheses.

The principal peak on the radial distribution curve of propane (Fig. 1, curve B), at 1.53 Å., represents the C–C bond distance. The small and accordingly unreliable peak representing the C–H distance has its maximum at 1.17 Å. The rest of the curve is compatible with a model with C–H ≅ 1.09 Å., C–C = 1.54 Å., and all angles close to the tetrahedral value 109°28′; the principal distances for this model, 10 C–H at 2.17 Å. and C–C at 2.51 Å., are represented by a peak at 2.23 Å. and an unresolved hump at about 2.5 Å.

Intensity curves calculated for the ratio C–H/C–C = 1.09/1.54 and for the values 109°28′, 111°30′, and 113°30′ for the C–C–C bond angle, the H–C–C angles being taken as 109°28′, are shown in Fig. 2. These curves all reproduce satisfactorily the appearance of the photographs;[11] the quantitative agreement with the 111°30′ curve is somewhat better than that for either of the others, however, permitting us to assign to the C–C–C angle the value 111°30′ ± 3°. The quantitative comparison[12] is ·shown in Table II; it leads to the value C–C = 1.54 ± 0.02 Å., with C–H = 1.09 Å. Wierl[8] reported C–C = 1.52 ±

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(7) J. D. Kemp and K. S. Pitzer, *J. Chem. Phys.*, **4**, 749 (1936); THIS JOURNAL, **59**, 276 (1937); J. B. Howard, *Phys. Rev.*, **51**, 53 (1937).

(8) R. Wierl, *Ann. Physik*, **13**, 453 (1932).

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

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

(11) The apparent faint first ring on the photographs is not represented by a very well-defined peak on the curves.

(12) The values given by the first and fifth maxima have been omitted in taking the average. The reason for the poor agreement shown by the fifth maximum is not known to us.

0.05 Å., assuming C–H = 1.10 Å. and all angles tetrahedral, from the measurement of photographs showing four rings. Bauer,[13] using his analytic method of interpretation, reported C–C = 1.50 Å., C–H = 1.08 Å., and the angle C–C–C = 114°; we believe that these values are somewhat less reliable than those found in the present investigation, partly because our new photographs are better than those used by Bauer.

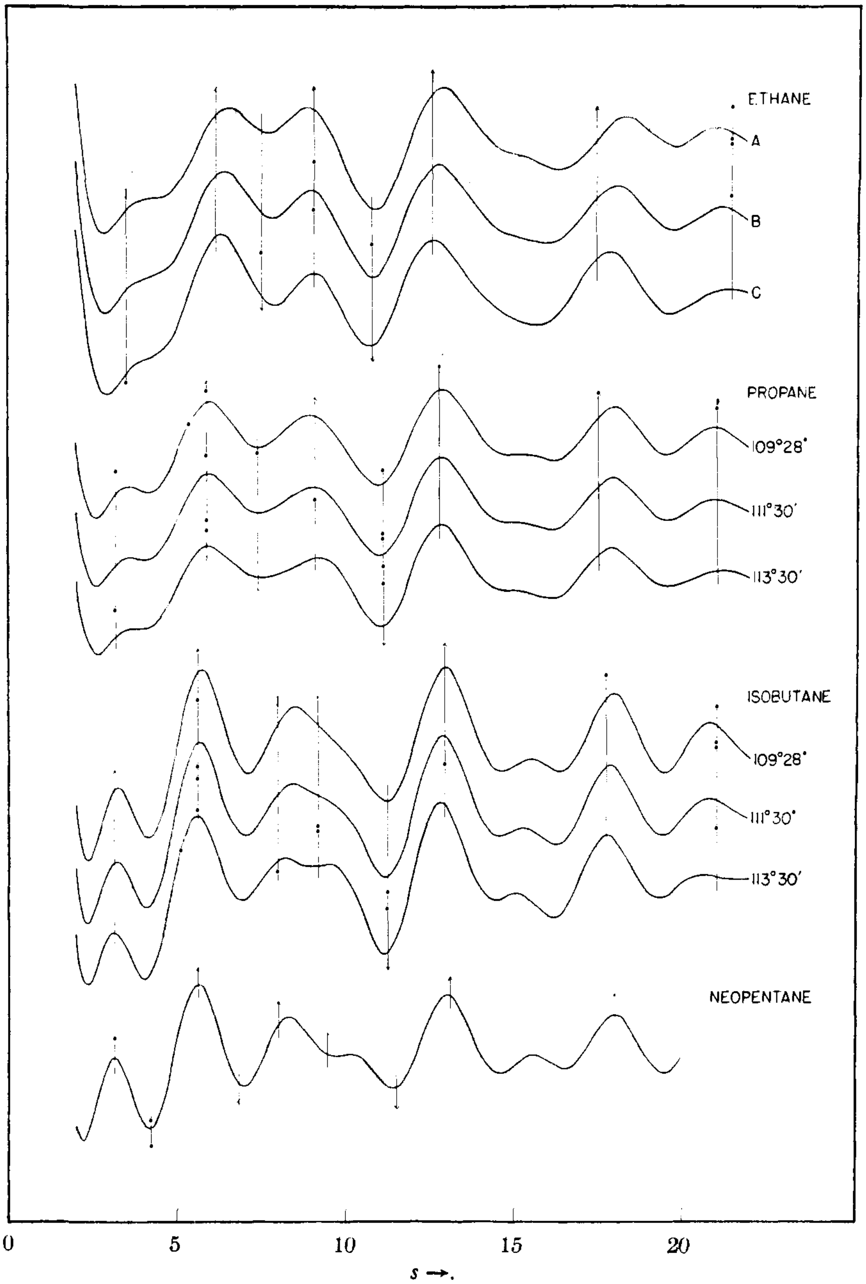

Fig. 2.—Theoretical intensity curves for ethane, propane, isobutane and neopentane. The arrows show the positions of the maxima and minima measured on the photographs.

The radial distribution function for isobutane (Fig. 1, curve C) shows well-defined peaks at 1.13, 1.54, and 2.53 Å., and indications of a distance 2.2 Å. also. The peak at 1.54 Å. represents the C–C bond distance, and that at 2.53 Å. the larger C–C distance, the ratio of these corresponding to the value 110°30' for the C–C–C bond angle.

Intensity curves calculated for C–H = 1.09 Å., C–C = 1.54 Å., angles H–C–C = 109°28', and angles C–C–C = 109°28', 111°30', and 113°30', shown in Fig. 2, agree well in general with the appearance of the photographs, as indicated by the data in Table III; there can also be seen on the photographs a faint ring (too faint to be measured) between the fourth and fifth maxima of the table, corresponding to the small peak on the curves. The C–C–C bond angle can be evaluated with use of the third ring and its shelf, for which we estimate the intensity ratio 3/2, which corresponds to the 111°30' curve. The quantitative comparison with this curve leads to the average value C–C = 1.54 ± 0.02 Å., with the angle C–C–C equal to 111°30' ± 2°.

The photographs of neopentane show five rings, the third of which has an outer shelf; the general appearance of the photographs is closely indicated by the calculated intensity curve shown in Fig. 2. (A faint ring, not included in the table, can be seen at about s = 15.5.) The radial distribution curve corresponding to the measured s_0

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(13) S. H. Bauer, *J. Chem. Phys.*, **4**, 407 (1936).

TABLE II

PROPANE

Max.	Min.	I	s_0	s^a	C-C, Å.
1		1	3.18	3.63	(1.76)
2		4	5.87	5.93	1.556
	3		7.40	7.40	1.540
3		3	9.11	9.09	1.537
	4		11.13	11.03	1.526
4		3	12.78	12.85	1.548
5		2	17.51	17.94	(1.577)
6		1	21.09	21.04	1.536
				Average	1.541 Å.

[a] Calculated for the model with C–H = 1.09 Å., C–C = 1.54 Å., and the angle C–C–C = 111°30′.

TABLE III

ISOBUTANE

Max.	Min.	I	s_0	s^a	C-C, Å.
1		1	3.13	3.22	(1.58)
2		5	5.60	5.66	1.557
3		3	7.97	8.43	(1.63)
Shelf		2	9.17		
	4		11.25	11.19	1.532
4		4	12.94	12.89	1.534
5		3	17.77	17.87	1.549
6		2	21.12	20.83	1.519
				Average	1.538 Å.

[a] Calculated for the model with C–H = 1.09 Å., C–C = 1.54 Å., angles H–C–C = 109°28′, and angles C–C–C = 111°30′.

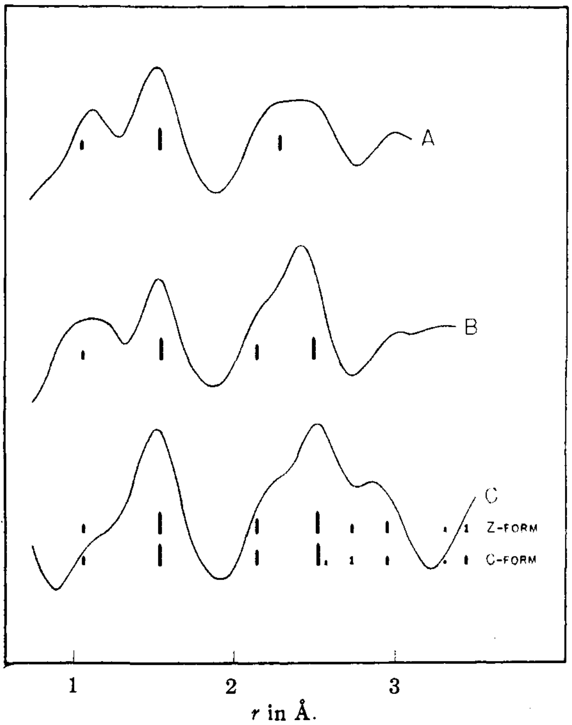


Fig. 3.—Radial distribution curves for (A) cyclopropane, (B) cyclopentane and (C) cyclohexane.

and I values given in Table IV (Fig. 1, curve D) shows peaks at 1.09, 1.53, and 2.52 Å., and humps indicating distances about 2.15 and 2.95 Å. The C–C bond distance is given directly by the 1.53 Å. peak as 1.53 Å., and by the 2.52 Å. peak as 1.54 Å.

TABLE IV

NEOPENTANE

Max.	Min.	I	s^0	s	C-C, Å.
1		1	3.12	3.17	(1.565)
	2		4.22	4.20	1.533
2		4	5.60	5.62	1.545
	3		6.84	6.97	1.559
3		3	8.00	8.32	(1.60)
Shelf		1	9.44	10.08	(1.64)
	4		11.50	11.42	1.533
4		4	13.10	13.00	1.532
5		2	18.02	18.00	1.539
				Average	1.540 Å.

The quantitative comparison of s_0 values and s values calculated for the tetrahedral model with C–H = 1.09 Å. and C–C = 1.54 Å. leads to C–C = 1.54 ± 0.02 Å., the inner ring being ignored as usual and the third ring with its shelf omitted from consideration because of its unsymmetrical shape.

The photographs of neopentane provide some information regarding the orientation of methyl groups in this molecule. There are two configurations with non-rotating methyl groups which preserve holohedral tetrahedral symmetry for the molecule; in these the methyl groups are oriented with their C–H bonds in the planes determined by the central carbon atom and two other carbon atoms, with the hydrogen atoms of each methyl group either *cis* or *trans* to the other methyl groups. Intensity curves calculated for both of these configurations are unsatisfactory, in that they show a pronounced maximum between the third and fourth rings on the photographs, where only a shelf is observed. It is possible that the configuration obtained by rotating each methyl group through 30° from either of the two orientations described above, which causes the hydrogen atoms of different methyl groups to fit together like cogs, would be considered satisfactory; its curve shows a shelf on the third ring and is otherwise like the photographs except that the peak at about s = 15.5 is too large. The average curve calculated for 30° intervals in azimuthal angle for each methyl group, simulating free rotation, is, on the other hand, completely satisfactory (Fig. 2).

It was noticed that the longer C–H distances are of little importance in the curve for the free-rotation model; the curve calculated by ignoring all C–H terms except those for the bond distance and the next larger distance (which is unchanged by rotation) is qualitatively indistinguishable from the free-rotation curve, and the s values for the peaks of the two curves differ on the average by only 0.02. In our treatment of propane and isobutane we have made use of this simplification.

Cyclopropane, Cyclopentane, and Cyclohexane.—The sample of cyclopropane used was provided by Professor G. S. Parks of Stanford University. Of the two samples of cyclopentane photographed, one was prepared for us by Dr. G. W. Wheland by the catalytic hydrogenation of cyclopentadiene and the other was provided by Mr. T. A. Boyd of the General Motors Research Laboratory. Kahlbaum cyclohexane was used with no further purification.

Cyclopropane gave photographs showing four rings, with qualitative appearance corresponding closely to the calculated curve of Fig. 4. The s_0 and I values given in Table V lead to the radial distribution curve shown in Fig. 3 (curve A), with peaks at 1.12 Å. (C–H bond distance), 1.52 Å. (C–C bond distance) and 2.2–2.5 Å. (larger C–H distance). The intensity curve of Fig. 4 is calculated for a model with the three carbon atoms at the corners of a regular triangle and the hydrogen atoms at tetrahedron corners out of the plane of the carbon ring, the H–C–H angle being taken as 109°28′ and the C–C and C–H distances in the ratio 1.54/1.09. With omission of the inaccurate readings for the first maximum, second minimum and the broad third maximum, the carbon–carbon distance is found to have the value 1.53 ± 0.03 Å.[14]

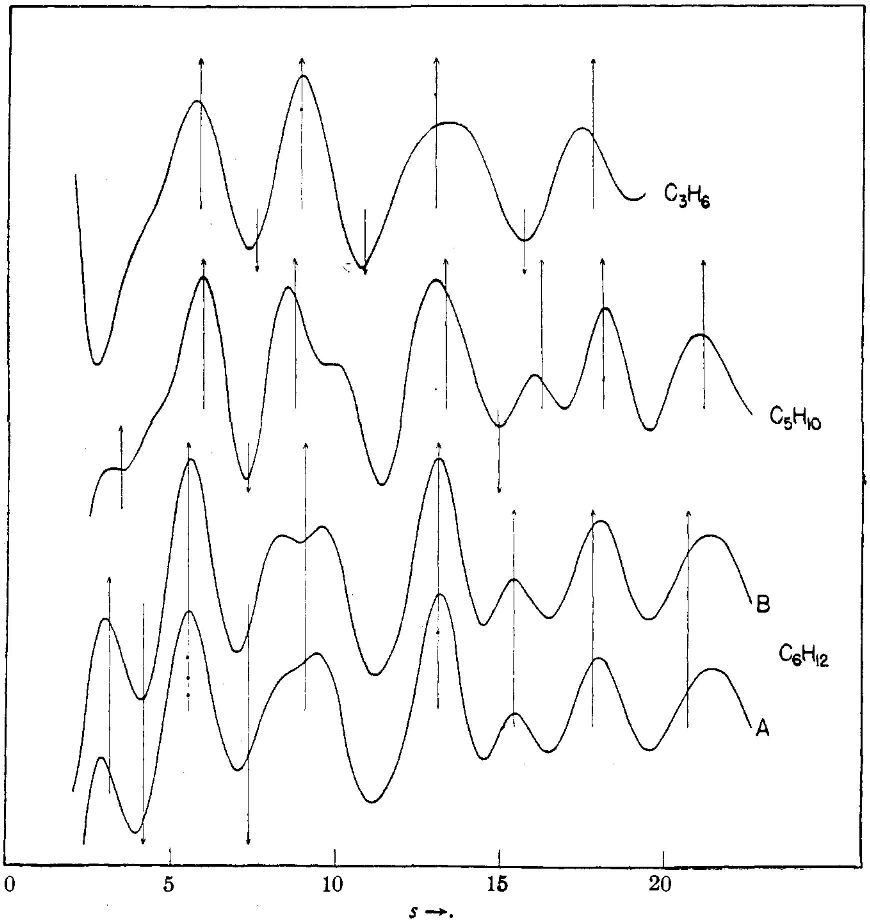


Fig. 4.—Theoretical intensity curves for cyclopropane, cyclopentane and cyclohexane.

TABLE V

CYCLOPROPANE

Max.	Min.	I	s_0	s	C–C, Å.
1		4	5.83	5.72	(1.51)
	2		7.55	7.30	(1.48)
2		4	8.90	8.92	1.543
	3		10.84	10.70	1.519
3		3	13.00	13.46	(1.59)
	4		15.69	15.62	1.532
4		2	17.77	17.42	1.509
				Average	1.526 Å.

The photographs of cyclopentane have the general appearance indicated by the calculated curve of Fig. 4. The shelf on the third ring, which can barely be seen on the photographs, seems to be displaced outward, however, the fourth minimum appearing flat rather than sharp; neither of the two corresponding s_0 values could be measured reproducibly. The estimated relative intensities

(14) In a note added at the end of his last paper[8] Wierl stated that he had found for the carbon–carbon distance in cyclopropane the value 1.6 ± 0.1 A.

of the last three rings do not correspond well with those shown by the curve.

The radial distribution curve (Fig. 3, curve B) corresponding to the s_0 and I values of Table VI has peaks at 1.1, 1.53, and 2.42 Å., the first two representing the C–H and C–C bond distances. The comparison of s_0 and s values for a model based on a regular plane pentagon of carbon atoms, with C–C = 1.54 Å. and C–H = 1.09 Å., leads to the averaged result C–C = 1.52 ± 0.03 Å., in good agreement with Wierl's value[8] 1.51 ± 0.08 Å.

TABLE VI

CYCLOPENTANE

Max.	Min.	I	s_0	s	C–C, Å.
1		1	3.44	3.11	(1.40)
2		5	5.98	5.94	1.528
	3		7.28	7.20	1.523
3		5	8.72	8.50	1.500
Shelf		1	11.12		
4		4	13.30	12.91	1.500
	5		14.86	14.84	1.539
5		2	16.20	15.95	1.516
6		2	18.10	18.07	1.546
7		2	21.40	20.94	1.507
				Average	1.520 Å.

The s_0 and I values for the photographs of cyclohexane (Table VII), showing seven rings, lead to the radial distribution curve represented in Fig. 3 (curve C). The two principal peaks are at 1.52 and 2.51 Å., corresponding closely to the values 1.54 and 2.51 Å. expected for single-bonded carbon atoms at tetrahedral angles. Intensity curves calculated for C–C = 1.54 Å., C–H = 1.09 Å., and all bond angles 109°28′ are given in Fig. 4, A representing the Z form (staggered ring) and B the C form. These reproduce reasonably well the appearance of the photographs except in the neighborhood of the third ring, which is observed as a rather broad ring with a faint outer shelf. Except for the presence of the shelf, the appearance of the third ring is about as expected for model A, whereas for model B a resolved double peak would be seen; otherwise the two curves are equally suitable. The quantitative comparison for model A is shown in Table VII. The average of the more reliable values for the carbon–carbon bond distance is 1.540 Å.; considering also the radial distribution result, we write for cyclohexane C–C = 1.53 ± 0.03 Å., in approximate agreement with the value 1.51 ± 0.03 Å. reported by Wierl[15] from the measurement of photographs showing four rings.

TABLE VII

CYCLOHEXANE

Max.	Min.	I	s_0	s[a]	C–C, Å.
1		3	3.08	2.85	(1.43)
	2		4.13	3.89	(1.45)
2		10	5.48	5.47	1.538
3		3	9.03	9.37	(1.59)
Shelf		0.5	11.14		
4		4	13.07	13.08	1.540
5		1	15.38	15.34	1.536
6		2	17.78	17.86	1.547
7		1	20.69	21.35	(1.589)
				Average	1.540 Å.

[a] Calculated for the model consisting of a staggered ring in the Z-configuration with C–C = 1.54 Å., C–H = 1.09 Å. and all bond angles 109°28′.

Allene.—A sample of allene was kindly given us by Dr. W. E. Vaughan of Harvard University. Electron diffraction photographs of this substance were found to show four well-defined rings, the first having a noticeable outer shelf, the second a pronounced outer shelf or subsidiary ring, and the third a faint outer shelf (not measured).

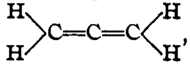
The measured ring diameters and estimated intensity values given in Table VIII (averages for eleven photographs) lead to the radial distribution curve shown in Fig. 5 (curve A). The structure of allene,  $\mathrm{H_2C{=}C{=}CH_2}$, is determined by three significant parameters, the C=C bond distance, the C–H bond distance, and the H–C–H bond angle. Of the five interatomic distances (other than H–H) in the molecule, the C=C bond distance contributes twice as much to the diffraction pattern as any other; its value is given by the principal peak, at 1.34 Å., in the radial distribution curve. Without doubt the C–H bond distance is close to 1.06 Å. and the H–C–H bond angle to 109°28′; the interatomic distances corresponding to these values and to C=C = 1.34 Å. agree well with the radial distrib-

TABLE VIII

ALLENE

Max.	Min.	I	s_0	s[a]	C–C, Å.
1		10	5.92	5.93	1.342
1a		2	7.26		
	2		8.77	8.57	(1.309)
2		5	9.93	9.95	1.343
2a		2	12.00	11.65	(1.301)
3		4	15.04	15.05	1.341
4		2	19.50	19.36	1.331
				Average	1.339 Å.

[a] Calculated for the model with C=C = 1.34 Å., C–H = 1.06 Å. and the angle H–C–H = 109°28′.

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(15) R. Wierl, *Ann. Physik*, **8**, 521 (1931).

ution curve, the C–H bond distance (1.06 Å.) appearing as a hump on the first peak, the C–H and C–C distances 2.11 and 2.68 Å. appearing only partially resolved at 2.25 and 2.60 Å., and the longest C–H distance 3.40 Å. appearing as a separate peak at 3.40 Å.

Verification of this structure is provided by the comparison with calculated intensity curves. In Fig. 6 curve A represents the model described above and curve B a similar model with the C=C bond distance equal to 1.38 Å., as given by the original table of covalent radii. Each of these curves reproduces closely the qualitative aspect of the photographs; curve A also shows quantitative agreement, whereas curve B shows a systematic difference of about 3%. The quantitative comparison of measured ring diameters and s values for the maxima and minima of curve A is shown in Table VIII. The mean of the values given for the C=C distance by the four principal maxima is 1.339 Å. A similar comparison for the four principal maxima with curve B gives 1.346 Å. Considering also the radial distribution value 1.34 Å., we accept for the C=C double-bond distance in allene the value 1.34 ± 0.02 Å.; the C–H distance was assumed to be within 0.04 Å. of 1.06 Å. and the H–C–H bond angle close to 109°28′, their independent evaluation being impossible because of the small contribution of the C–H terms to the diffraction pattern.

Our result agrees approximately with that of Wierl,[8] who found the value C=C = 1.31 ± 0.05 Å. from measurement of two rings.

Ethylene.—Photographs of ethylene were found to show five rings, of uniformly decreasing intensity except for the third, which is weak and appears as an outer shelf on the second. The radial distribution curve calculated with the s_0 and I values in Table IX (Fig. 5, curve B) shows only two peaks, the first, at 1.32 Å., representing the C=C bond distance with the C–H bond appearing as a hump, and the second, at 2.14 Å., the longer C–H distance.

The calculated intensity curves A, B, and C in Fig. 6 are for coplanar models with the ratios 1.06/1.38, 1.09/1.38, and 1.12/1.38, respectively, for C–H/C=C, the H–C–H bond angle being given the reasonable value 109°28′. Curve B reproduces the appearance of the photographs closely; it shows a small defect in that the third ring is about equidistant from the second and

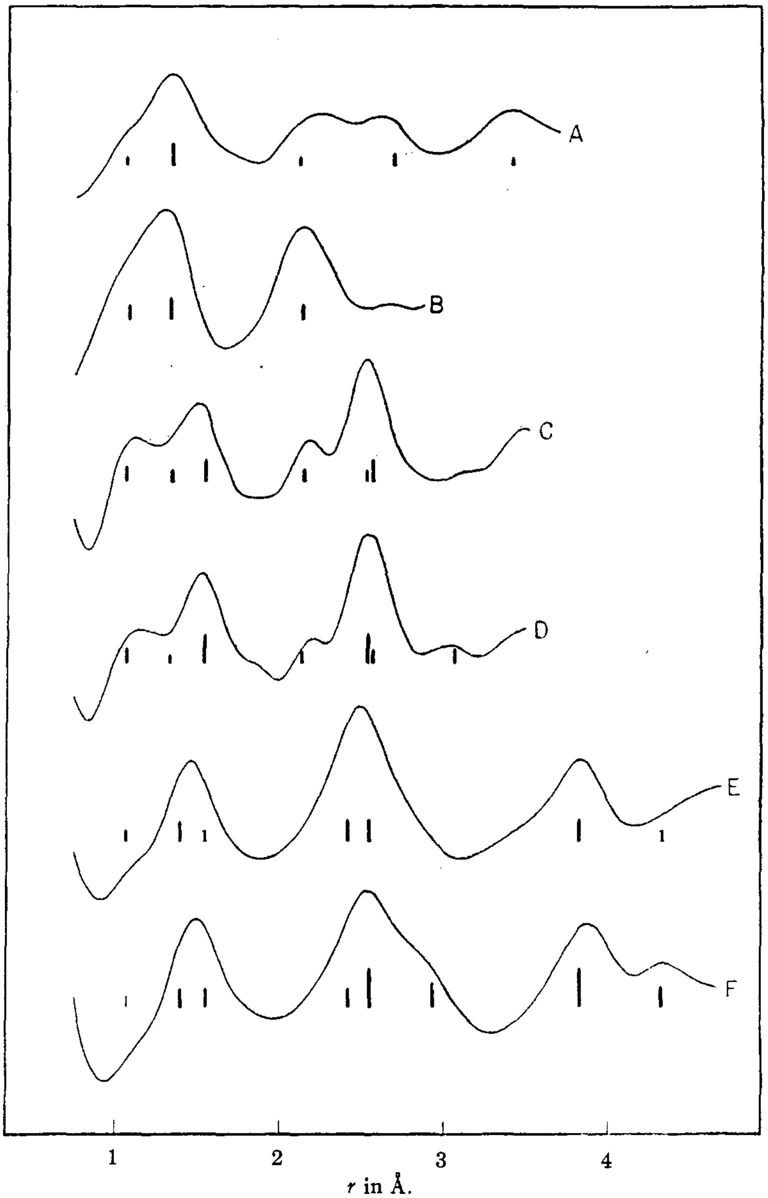

Fig. 5.—Radial distribution curves for (A) allene, (B) ethylene, (C) isobutane, (D) tetramethylethylene, (E) mesitylene and (F) hexamethylbenzene.

fourth, rather than closer to the second as observed. Curve A is unsatisfactory because of the further shift of the third ring toward the fourth, and curve C because it gives the third ring too great intensity. The effect of increase in H–C–H bond angle is to shift the third ring toward the fourth, as is seen from curve D, which is similar to B except for increase in the angle to 115°; this curve and similar curves for 120 and 125° are all unsatisfactory for this reason.

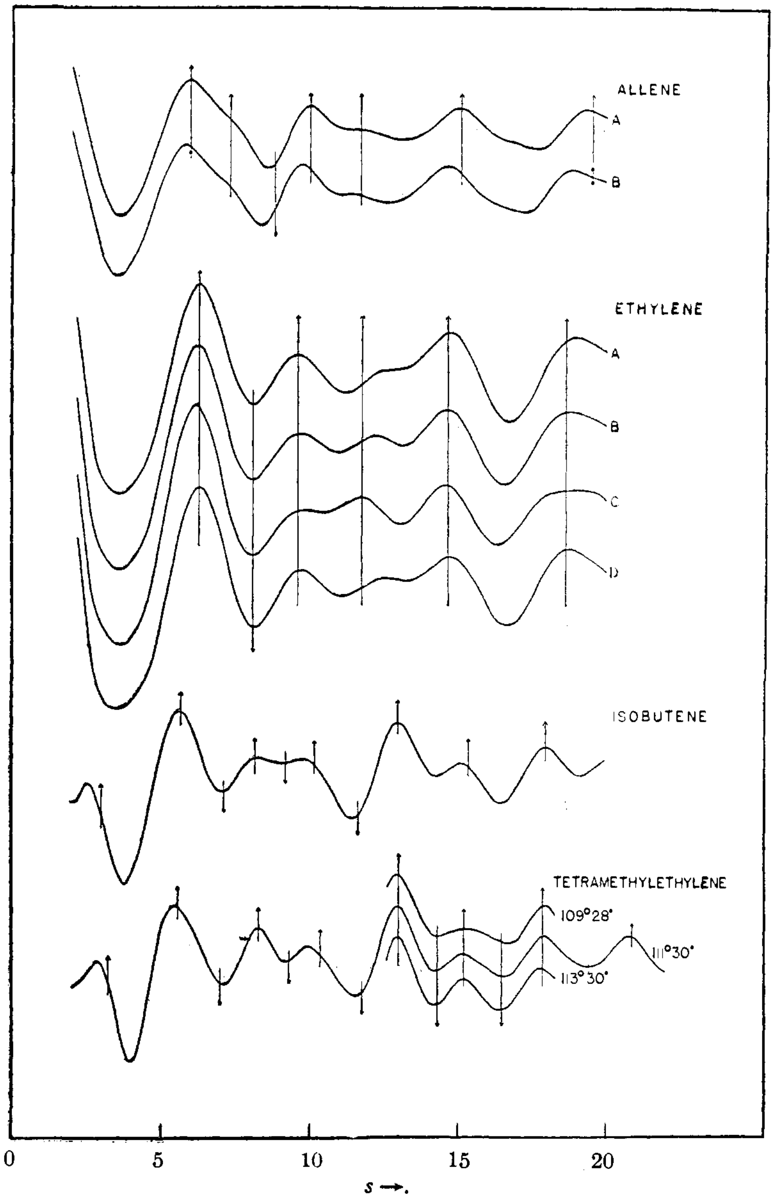

Fig. 6.—Theoretical intensity curves for allene, ethylene, isobutene and tetramethylethylene. The s-scale for ethylene has been decreased by 3%, to show the quantitative agreement between the measured s values and the curve with C=C = 1.34 Å.

Quantitative comparison of s_0 and s values for model B (Table IX) leads to C=C = 1.34 ± 0.02 Å. and C–H = 1.06 ± 0.03 Å., the H–C–H bond angle having the value 110 ± 5°. This model agrees well with the radial distribution curve; the peak at 1.32 Å. represents the distances 1.06 and 1.34 Å. only partially resolved, and the peak at 2.14 Å. occurs at exactly the place required by the 110° model. Wierl[8] reported C=C = 1.30 ± 0.10 Å. from measurement of two rings on his photographs.

The structure which we assign to ethylene corresponds to the values 33.7, 28.7, and 5.0 × 10^{-40} for the three principal moments of inertia of the molecule. These are in reasonably good agreement with the values 33.2, 27.5, and 5.7 × 10^{-40} found spectroscopically by Badger,[16] and the single value 28.85 × 10^{-40} reported by Scheib and Lueg.[17] Penney[18] has recently interpreted Badger's values as corresponding to the distances C–H = 1.08 Å. and C=C = 1.33 Å. and the angle H–C–H = 118°. Our photographs are compatible with these distances but suggest a smaller value for the angle.

Isobutene and Tetramethylethylene.—Using a sample of isobutene provided by Professor H. J. Lucas of these Laboratories and a sample of tetramethylethylene provided by Professor G. B. Kistiakowsky and Dr. W. E. Vaughan of Harvard University, we obtained photographs showing seven or eight rings, with the average s_0 values and estimated intensities given in Tables X and XI. The radial distribution curves (Fig. 5, curves C and D) for the two substances are compatible with the double-bond and single-bond distances C=C = 1.34 Å. and C–C = 1.54 Å., but because of lack of resolution of the peaks the values are not verified individually.

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(16) R. M. Badger, *Phys. Rev.*, **45**, 648 (1934).

(17) W. Scheib and P. Lueg, *Z. Physik*, **81**, 764 (1933).

(18) W. G. Penney, *Proc. Roy. Soc.* (London), **A158**, 306 (1937).

TABLE IX

ETHYLENE

Max.	Min.	I	s_0	s[a]	C–C, Å.
1		6	6.46	6.22	1.329
	2		8.30	8.10	1.346
2		3	9.90	9.68	1.349
3		1	12.07	12.17	(1.391)
4		2	15.07	14.62	1.339
5		1	19.08	18.76	1.356
				Average	1.344 Å.

[a] Calculated for the model with C=C = 1.38 Å., C–H = 1.09 Å. and the angle H–C–H = 109°28′.

TABLE X

ISOBUTENE

Max.	Min.	I	s_0	s[a]	s/s_0
1		1	2.99	2.66	(0.89)
2		10	5.69	5.68	0.998
	3		7.10	7.02	.989
3		2	8.15	8.29	1.017
	4		9.20	9.20	1.000
4		2	10.14	9.90	0.976
	5		11.66	11.65	.999
5		3	13.00	13.05	1.004
6		1	15.39	15.40	1.001
7		2	18.03	18.04	1.001
				Average	0.998
				C–C =	1.537 Å.
				C=C =	1.337 Å.

[a] Calculated for the model with C–H = 1.09 Å., C–C = 1.54 Å., C=C = 1.34 Å., angle C–C–C = 111°30′, and angles H–C–C = 109°28′.

TABLE XI

TETRAMETHYLETHYLENE

Max.	Min.	I	s_0	s[a]	s/s_0
1		1	3.22	2.87	(0.88)
2		6	5.52	5.43	0.984
	3		6.95	7.06	1.016
3		3	8.24	8.31	1.009
	4		9.27	9.20	0.992
4		2	10.31	9.92	(.962)
	5		11.71	11.51	.983
5		4	12.95	12.92	.998
	6		14.27	14.23	.997
6		1	15.19	15.15	.997
	7		16.43	16.48	1.003
7		2	17.85	17.85	1.000
8		$^1/_2$	20.86	20.76	0.995
				Average	0.998
				C–C =	1.537 Å.
				C=C =	1.337 Å.

[a] Calculated for the model with C–H = 1.09 Å., C–C = 1.54 Å., C=C = 1.34 Å., angles C–C–C = 111°30′, and angles H–C–C = 109°28′.

Calculated intensity curves are shown in Fig. 6. For each substance there is shown a complete curve calculated for the distances C–H = 1.09 Å., C–C = 1.54 Å. and C=C = 1.34 Å. and the angles H–C–C = 109°28′ and C–C–C = 111°30′; in addition there are shown for tetramethylethylene segments of curves for models similar to this except for the value of the angle C–C–C, which is changed to 109°28′ and to 113°30′, the curves being appreciably different from the 111°30′ curve only in the region covered by these segments. The estimated intensities of the three rings in this region are 4, 1, and 2; it is seen that these correspond more closely to the 111°30′ curve than to either of the other two, so that we obtain for the C–C–C bond angle the value 111° 30′ ± 2°. This evaluation of the bond angle is not invalidated by a change of as much as 0.04 Å. in the assumed C=C distance.

A similar determination of the bond angle for isobutene cannot be carried out, the curves being practically unchanged by a change of 2° in the angle. It is of course probable that the angle has the same value in this substance as in tetramethylethylene.

The calculated intensity curves are changed in shape only very slightly by changing C=C from 1.34 to 1.38 Å., so that the carbon–carbon double-bond distance in these substances cannot be evaluated independently. We think that the value is within 0.02 of 1.34 Å.; if we were to assume 1.38 Å., the values quoted below for the carbon–carbon single-bond distance would be decreased to 1.52 Å. for isobutene and 1.53 Å. for tetramethylethylene.

The quantitative comparison of s_0 and s shown in Tables X and XI leads to 1.54 ± 0.02 Å. for the C–C distance in each of the two substances, the value 1.34 Å. for C=C being assumed. No other investigation of interatomic distances in these hydrocarbons has been reported.

Mesitylene and Hexamethylbenzene.—Photographs showing eight or nine rings were prepared of mesitylene, provided by Dr. W. E. Vaughan, and of hexamethylbenzene (Eastman Kodak Co.), with s_0 and I values given in Tables XII and XIII.

There is little doubt that the C–C distance in the benzene ring retains in its methyl derivatives the value 1.39 Å. found for benzene itself.[19] The main question regarding these substances is whether the distance from methyl carbon to ring carbon is determined by the usual single-bond radius, having thus the value 1.54 Å., or whether

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[19] R. Wierl, ref. 15: Pauling and Brockway, *J. Chem. Phys.*, **2**, 867 (1936). V. Schomaker, working in these Laboratories, has recently obtained benzene photographs with rings extending to s = 20 which leads to C–C = 1.39 Å. This value has also been substantiated to within 0.03 Å. by the interesting investigation of the phthalocyanines by J. M. Robertson, *J. Chem. Soc.*, 1195 (1936).

TABLE XII

MESITYLENE

Max	Min.	I	s_0	s^a	s/s_0
1		4	3.32	3.12	(0.94)
	2		4.34	4.23	(.975)
2		10	5.54	5.48	.989
	3		7.39	7.18	(.972)
3		3	8.60	8.79	1.022
	4		9.43	9.39	0.996
4		4	10.33	10.22	.989
5		$^1/_2$	11.59	11.88	(1.025)
6		4	13.49	13.58	1.007
7		1	15.30	15.06	0.984
8		2	18.31	18.60	1.016
				Average	1.000

$C_{ar}-C_{al} = 1.540$ Å.
$C_{ar}-C_{ar} = 1.390$ Å.

[a] Calculated for the model with $C_{ar}-C_{ar} = 1.39$ Å., $C_{ar}-C_{al} = 1.54$ Å. and C–H = 1.09 Å.

TABLE XIII

HEXAMETHYLBENZENE

Max.	Min.	I	s_0	s^a	s/s_0
1		4	3.27	3.15	(0.964)
	2		4.21	4.13	(.981)
2		10	5.30	5.34	1.008
Shelf		1	6.24		
	3		7.04	7.16	(1.017)
Shelf		1	7.61		
3		4	8.76	8.86	1.011
	4		9.51	9.52	1.001
4		4	10.29	10.22	0.993
5		$^1/_2$	11.80	12.08	(1.023)
6		4	13.31	13.42	1.008
7		1	15.16	15.20	1.003
8		2	18.25	18.22	0.998
9		$^1/_2$	20.35	20.20	.993
				Average	1.002

$C_{ar}-C_{al} = 1.543$ Å.
$C_{ar}-C_{ar} = 1.393$ Å.

[a] Calculated for the model with $C_{ar}-C_{ar} = 1.39$ Å., $C_{ar}-C_{al} = 1.54$ Å. and C–H = 1.09 Å.

it is the sum of the radius 0.77 Å. for an aliphatic carbon atom and the radius 0.70 or 0.71 Å. for an aromatic carbon atom, giving the value $C_{ar}-C_{al} = 1.47$ or 1.48 Å., as suggested originally by Mrs. Lonsdale.[4] Accepting a value close to 1.09 Å. for C–H, we thus have two principal models to be tested, one (model A) with $C_{ar}-C_{al} = 1.54$ Å. and the other (model B) with $C_{ar}-C_{al} = 1.48$ Å., both having $C_{ar}-C_{ar} = 1.39$ Å.

The radial distribution curves, shown in Fig. 5 (curves E and F), support model A rather than B. For example, the first peak for hexamethylbenzene, at 1.49 Å., lies closer to the value given by A, 1.47 Å. (the mean of 1.39 Å. and 1.54 Å. contributing equally), than to that given by B, 1.43 Å.; and the second peak, at 2.53 Å., also lies closer to the value given by A for the principal interatomic distance in this region, 2.54 Å., than to that given by B, 2.48 Å. For mesitylene these peaks are observed at 1.46 and 2.49 Å., the expected values for A being 1.44 and 2.48 Å. and for B 1.42 and 2.45 Å. These four peaks thus have values greater than expected by an average amount of only 0.01 Å. for model A, and of 0.05 Å. for model B.

The qualitative aspect of the photographs also supports model A. On the photographs of hexamethylbenzene there is observed between the fourth and sixth rings a very weak fifth ring, with apparent intensity estimated to be about one-eighth as great as for its neighbors. A corresponding small peak appears on the intensity curve calculated for model A (Fig. 7), but not on that for model B. The appearance of the photographs is in general well reproduced by curve A; in particular, mention may be made of the shelves adjacent to the third minimum.

The quantitative comparison of measured s_0 values and s values calculated for models A for mesitylene and hexamethylbenzene is given in Tables XII and XIII. With omission of the innermost maximum and minimum, the unreliable third minimum, and the very weak fifth maximum for each substance, the average values $s_A/s_0 = 1.000$ and 1.002, respectively, are found. These correspond to the interatomic distances $C_{ar}-C_{al} = 1.54 \pm 0.01$ Å. and $C_{ar}-C_{ar} = 1.39$ Å. in both substances, the $C_{ar}-C_{al}$ distance being equal to the single-bond distance in aliphatic compounds and the $C_{ar}-C_{ar}$ distance to that in benzene to within the probable error of the determination.

In her X-ray study of crystals of hexamethylbenzene[4] Mrs. Lonsdale found the value $C_{ar}-C_{al} = 1.48$ Å. to be in better agreement with the observed intensities than the value 1.42 Å.; her work provides no evidence against the value 1.54 Å., however, which she did not test.

An electron-diffraction study of benzene, *p*-xylene, mesitylene, and hexamethylbenzene has been made recently by Jones,[20] who, on the basis of measurements extending to $s_0 = 14$, reported the values $C_{ar}-C_{al} = 1.50 \pm 0.01$ Å. and $C_{ar}-C_{ar} = 1.40 \pm 0.01$ Å. Jones' s_0 values are about 1.3% greater than ours, and comparison of them with our calculated values of s_A leads to

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(20) P. L. F. Jones, *Trans. Faraday Soc.*, **31**, 1036 (1935).

$C_{ar}-C_{al}$ = 1.52 Å. and $C_{ar}-C_{ar}$ = 1.37 Å., these distances being 0.02 Å. smaller than those given by our photographs. The rings given by mesitylene and hexamethylbenzene are unusually sharp and well defined, and we estimate, by comparison with other substances for which the electron-diffraction method has been tested,[21] that the error in our values of s_0 is not greater than about 0.5%.

Summary of Results

Values of interatomic distances and bond angles found in this investigation are collected in Table XIV. It should be mentioned that Wierl's early electron-diffraction work seems to be more reliable than he considered it to be; the mean difference of his C–C values and ours for the six hydrocarbons common to the two investigations is 0.03 Å., much less than the mean of the errors assigned by him, 0.07 Å.

The results shown in the table provide further evidence of the extraordinary extent to which the tetrahedral carbon atom of van't Hoff and Le Bel determines the structure of organic molecules. The values found for the angle between two single carbon–carbon bonds are in all cases (except cyclopropane) within 2° of the theoretical value 109°28′.

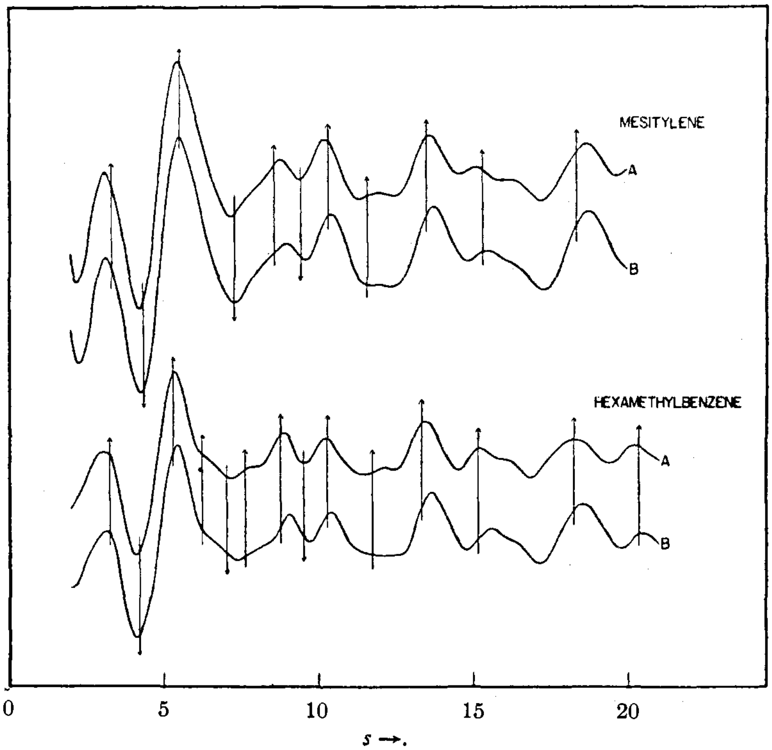

Fig. 7.—Theoretical intensity curves for mesitylene and hexamethylbenzene.

TABLE XIV

INTERATOMIC DISTANCES AND BOND ANGLES IN HYDROCARBONS

	C–H. Å.	C–C. Å.	C═C. Å.	Angle C–C–C
Ethane	1.09 ± 0.03	1.55 ± 0.03		
Propane	(1.09)[a]	1.54 ± .02		111°30′ ± 3°
Isobutane	(1.09)	1.54 ± .02		111°30′ ± 2°
Neopentane	(1.09)	1.54 ± .02		
Cyclopropane	(1.09)	1.53 ± .03		(60°)
Cyclopentane	(1.09)	1.52 ± .03		(108°)
Cyclohexane	(1.09)	1.53 ± .03		(110°)
Allene	(1.06)		1.34 ± 0.02	
Ethylene	1.06 ± 0.03		1.34 ± .02	
Isobutene	(1.09)	1.54 ± .02	(1.34)	(111°30′)
Tetramethylethylene	(1.09)	1.54 ± .02	(1.34)	111°30′ ± 2°
Mesitylene	(1.09)	1.54 ± .01		
Hexamethylbenzene	(1.09)	1.54 ± .01		

[a] Values enclosed in parentheses were assumed.

The Constancy of the Carbon–Carbon Single-Bond Distance.—For the eleven hydrocarbons containing carbon–carbon single bonds studied in this investigation the values found for the corresponding interatomic distance lie between the limits 1.52 and 1.55 Å., all being equal to the diamond value 1.54 Å. to within their estimated probable errors. The results found for isobutene, tetramethylethylene, mesitylene, and hexamethylbenzene show definitely that the carbon–carbon single-bond distance is not affected by adjacent carbon–carbon double bonds[22] or aromatic nuclei, provided that the conditions for resonance across the single bond are not satisfied.

It has been reported recently[23] that the spectroscopic study of methylacetylene leads to the value 1.462 ± 0.005 Å. for the carbon–carbon single-bond distance in this substance. This is 0.08 Å. less than the value 1.54 Å. which we expect on the basis of the argument that constancy of the single-bond distance should be retained in the presence of an adjacent triple as well as of an adjacent double bond or aromatic nucleus. An electron-diffraction investigation of this substance is under way in these Laboratories.

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[21] Pauling and Brockway, *J. Chem. Phys.*, **2**, 867 (1936).

[22] It has been found that a carbon–oxygen double bond decreases the single-bond radius of the carbon atom involved: Pauling and Brockway, paper to be submitted to THIS JOURNAL.

[23] G. Herzberg, F. Patat and H. Verleger, *J. Phys. Chem.*, **41**, 123 (1937).

It might be expected that the strain in cyclopropane, in which the C–C–C bond angles are distorted from 109°28′ to 60°, would weaken the bonds and thus lead to an increase in the bond distance. This effect is not observed, however, the carbon–carbon distance in cyclopropane being the same as in the other hydrocarbons to within the accuracy of the investigation. There is even some small indication that the C–C distance in cyclic aliphatic hydrocarbons is slightly smaller (by about 0.01 Å.) than the normal distance, the three values reported being 1.53, 1.52, and 1.53 Å.

It may be pointed out that the carbon–hydrogen bond seems not to show the constancy of interatomic distance found for the carbon–carbon single bond. The spectroscopic value for methane, 1.09 Å., and the value found in ethane, 1.09 Å., are definitely larger than the accurately known spectroscopic value 1.06 Å. for acetylene and cyanogen. In the CH molecule the observed distance is 1.12 Å.; it is possible that here the bonding orbital of carbon is different (with more $2p$ character) from that for quadrivalent carbon. The radius of the hydrogen atom is apparently more variable than those of other atoms, perhaps because the spatial extent of the valence orbital is much smaller than for other atoms. In the hydrogen molecule the covalent radius of hydrogen is 0.37 Å. and in the hydrogen halides 0.27 to 0.29 Å. Other stable hydrogen compounds show values within these limits: 0.29 to 0.32 Å. in hydrocarbons, 0.31 in ammonia, 0.30 in water, and 0.31 in hydrogen sulfide; in spectroscopic hydrides such as CH interatomic distances are usually about 0.03 Å. larger than in stable molecules.

Revised Values of Double-Bond Covalent Radii.—This investigation has led to the value 1.34 Å. for the carbon–carbon double-bond distance, 0.04 Å. less than the value provided by the table of covalent radii.[1a,24] Five years ago, when this table was extended to multiple bonds, there were few reliable experimental data on which the selected values for double-bond and triple-bond radii could be based. The single-bond radii were obtained from the study of a large number of interatomic distances found experimentally by crystal-structure and spectroscopic methods. The spectroscopic value of the triple-bond radius of nitrogen (in N_2) was found to bear the ratio 0.79 to the single-bond radius, and this ratio was assumed to hold for other atoms also. For the double-bond radii no similarly reliable experimental value was at hand. Wierl had reported 1.30 ± 0.10 Å. for the carbon–carbon double-bond distance in ethylene and 1.31 ± 0.05 Å. for that in allene; these correspond to 0.85 for the ratio of double-bond distance to single-bond distance, whereas the much larger ratio 0.92 is given by the oxygen–oxygen distance 1.20 Å. observed for the normal $^3\Sigma$ state of the oxygen molecule, which might be expected to approximate closely to the double-bonded state. Under these circumstances it seemed sensible to interpolate between the triple-bond factor 0.79 and unity, and the value 0.90 for the double-bond factor was chosen.[25]

The new carbon–carbon double-bond distance corresponds to the value 0.87 for the double-bond factor. Moreover, there are now available three accurately known triple-bond distances; 1.204 for C≡C in acetylene, 1.154 Å. for C≡N in hydrogen cyanide, and 1.094 for N≡N in the nitrogen molecule, whereas five years ago only the last was known. The ratios of these distances to the corresponding sums of single-bond radii are 0.782, 0.785, and 0.781, respectively. We accordingly now select 0.78 as the value of the triple-bond factor. Revised covalent radii[26] for first-row atoms are given in Table XV.

TABLE XV

COVALENT RADII

	C	N	O	F
Single bond	0.77	0.70	0.66	0.64
Double bond	.67	.61	.57	.55
Triple bond	.60	.55	.51	
	Si	P	S	Cl
Single bond	1.17	1.10	1.04	0.99
Double bond	1.06	1.00	0.95	.90
Triple bond	0.99	0.93	.88	

It is probable that the factors for atoms other than first-row atoms have values somewhat different from 0.87 and 0.78. Because of the small tendency of these atoms to form multiple bonds,

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[24] M. L. Huggins, *Phys. Rev.*, **28**, 1086 (1926); L. Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934).

[25] Sidgwick in 1933 ("The Covalent Link in Chemistry," Cornell University Press, 1933, p. 82), accepting 1.32 Å. for the carbon–carbon double-bond distance as indicated by Wierl's work, adopted 0.86 for the double-bond factor and 0.77 for the triple-bond factor.

[26] The revision leads to a difference of 0.06 Å. between the interatomic distance in the normal oxygen molecule and the sum of the double-bond radii. This may be attributed to the presence of an unusual structure, consisting of a single bond plus two three-electron bonds. We assign this structure both to the normal $^3\Sigma$ state, with r_0 = 1.204 Å., and to the excited $^1\Sigma$ state, with r_0 = 1.223 Å., the two differing in the relative spin orientations of the odd electrons in the two three-electron bonds. We expect for the double-bonded $^1\Delta$ state the separation r_0 = 1.14 Å.

few pertinent interatomic-distance data are available. The observed distances[27] 1.86 Å. in P_2 and 1.49 Å. in PN correspond to 0.93 Å. for the triple-bond radius of phosphorus, indicating the value 0.85 for the triple-bond factor for the second row. We further suggest 0.91 for the second-row double-bond factor, from comparison with the first-row factors. Second-row radii calculated in this way are also included in Table XV.

Interatomic Distances and Resonance.—Two years ago[1b] we constructed an empirical curve showing the dependence of the carbon–carbon distance on bond type for single bond–double bond resonance, using data for diamond (1.54 Å., single bond), graphite (1.42 Å., one-third double bond), and benzene (1.39 Å., one-half double bond), and accepting 1.38 Å. for the pure double-bond distance. With the aid of this curve a number of conclusions were drawn regarding bond type in resonating molecules.

The decrease of 0.04 Å. in the double bond distance requires that the resonance curve be revised. It is fortunate that this revision invalidates none of the earlier conclusions, for the reason that only the part of the curve from 0 to 50% double-bond character was made use of, and the new curve does not differ appreciably from the old one in this region.

The new curve representing the dependence of carbon–carbon interatomic distance on double-bond character is shown in Fig. 8. As mentioned above, this curve does not differ appreciably from the old one up to 50% double-bond character, and in this region it may be used as before to determine bond type from measured interatomic distances. The change in the curve between 50 and 100% double-bond character enhances its value; the new curve can be used to determine bond type in this region also, where the old one was useless because of its small slope.

The most extensive application which was made of the resonance curve was to the carbon–chlorine bond in phosgene and the chloroethylenes. In the electron-diffraction study of these substances[28] the carbon–carbon and carbon–oxygen double-bond values 1.38 and 1.28 Å. were assumed; the question accordingly arises as to what effect the new double bond values would have on the carbon–chlorine distances. The new double-bond distances are smaller than the old by 0.04 Å. It is probable, however, that in the chlorine-substituted ethylenes the carbon–carbon distance is about 1.36 Å. and in phosgene the carbon–oxygen distance is about 1.26 Å., for the following reason. Conjugation of the unshared pair of a chlorine atom with the double bond gives the carbon–chlorine bond some double-bond character and at the same time gives the double bond some single-bond character, amounting to 20 or 30%. Reference to Fig. 8 shows that this corresponds to a distance about 0.02 Å. larger than the double-bond distance, and thus about 0.02 Å. smaller than the old double-bond distance. To make this decrease of 0.02 Å. in the models each atom would be moved in 0.01 Å. toward the midpoint of the two. This change would have only an inappreciable effect on the calculated intensity curves, so that the models accepted in the original investigation would still be acceptable after revision in this way. Considering the angles involved, we see that the revision leads to carbon–chlorine distances which differ from the original ones by less than 0.005 Å., a negligible amount; the conclusions reached regarding double-bond character of the carbon–chlorine bonds are accordingly still valid.

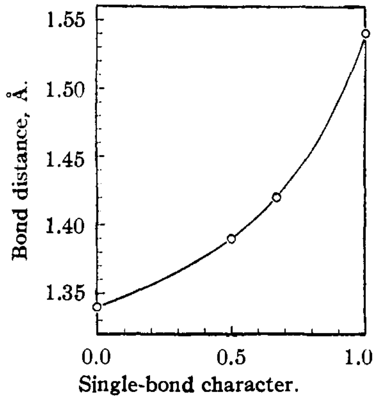

Fig. 8.—Curve showing the dependence of carbon–carbon bond distance on the relative degree of single-bond–double-bond character.

It is interesting that the resonance curve of Figure 8 can be represented by the equation

$$d = 1.54 - 0.20 \frac{3x}{(2x + 1)} \qquad (1)$$

in which x represents the double-bond character. This equation can be derived in the following simple way, based on Morse's interpretation of the

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[27] G. Herzberg, *Ann. Physik*, **15**, 677 (1932); J. Curry, L. Herzberg and G. Herzberg, *J. Chem. Phys.*, **1**, 749 (1933); *Z. Physik*, **86**, 348 (1933).

[28] L. O. Brockway, J. Y. Beach, and L. Pauling THIS JOURNAL, **57**, 2693 (1935).

curve.[29] Let the potential function for a resonating bond be given as the sum of two parabolas, representing single-bond and double-bond potential functions, with coefficients $1 - x$ and x

$$V(r) = (1 - x)C_1 (r - r_1)^2 + xC_2(r - r_2)^2 \qquad (2)$$

By equating to zero the differential of this with respect to r, we find the equilibrium distance as a function of x and the ratio of force constants C_2/C_1. For $C_2/C_1 = 3$, $r_2 = 1.34$, and $r_1 = 1.54$, this function is that given by Equation 1. The value 3 for the ratio of force constants is somewhat larger than that indicated by Badger's rule, which is about 2.3; it is probable that this increase is needed to compensate for the neglect of resonance energy in the assumed potential function.

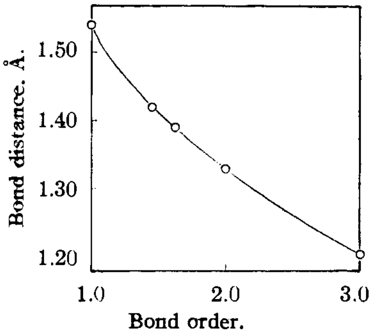

Fig. 9.—Curve showing the dependence of carbon–carbon bond distance on the order of bond (Penney).

In drawing the original resonance curve we pointed out that the assignment of 33.3% double-bond character to graphite and 50% to benzene is somewhat arbitrary; we selected the treatment leading to these numbers (division of valences of carbon among the available bonds) rather than a treatment based on a more complete quantum-mechanical discussion for the sake of simplicity, feeling that the discussion of resonance of molecules should be kept as close as possible to the accepted ideas and methods of chemistry. The arbitrariness of our procedure has again been pointed out by Penney,[18] who has introduced a new concept, that of the "order" of a bond. The order of a bond in a resonating molecule can be calculated by a quantum-mechanical method which is an extension of the valence-bond treatment applied in the calculation of resonance energies.[30] In benzene the bonds are of order 1.623, somewhat closer to double bonds (of order 2) than to single bonds (of order 1); this corresponds essentially to considering the resonance energy to increase the strength of the bonds. In graphite the bonds are found by a long calculation to be of order 1.45. Penney's curve relating interatomic distance to order of bond is shown in Fig. 9. It is very interesting that a simple curve passes through not only the four points represented in Fig. 8 but also the point 1.20 Å. at order 3 representing a triple bond; this becomes understandable when it is recognized that in a molecule containing equivalent bonds the order of the bonds is a measure of the total bond energy of the molecule, including resonance energy, since we might well expect a simple relation to hold between interatomic distance and bond energy for closely similar bonds.

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Summary

Values found for interatomic distances and bond angles in the thirteen hydrocarbons studied are given in Table XIV. The carbon–carbon single-bond distance is found to have the constant value 1.54 ± 0.02 Å., being unaffected by the presence of an adjacent double bond or benzene nucleus (provided that it does not form part of a conjugated system). The carbon–carbon double-bond distance in allene and acetylene has the value 1.34 Å. This is 0.04 Å. less than that formerly given by the table of covalent radii, which has accordingly been revised. The effect of the revision on the bond distance-resonance curve is discussed.

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(29) See footnote 3 of reference 1b.

(30) L. Pauling and G. W. Wheland, *J. Chem. Phys.*, **1**, 362 (1933).