steam and carbon.[19] This makes it appear that sodium carbonate catalyzes the formaldehyde-forming step: $C + H_2O \rightleftarrows C(H_2O)_{ads.} \rightleftarrows H_2CO$; according to this theory, sodium carbonate is a promoter for the catalytic activity of carbon, which by itself is able to decompose formaldehyde catalytically.[18] This mechanism for the acceleration of the steam–carbon reaction by sodium carbonate is in contrast to that of Kröger,[7] whose explanation involves a set of reactions completely divorced from the ordinary steam–carbon reaction.

Acknowledgment.—The author wishes to express his appreciation for the helpful criticism given by Dr. G. von Elbe, physical chemist, Central Experiment Station, U. S. Bureau of Mines, Pittsburgh, Pa.

Summary

1. Interpretation of available data on the steam–carbon reaction corroborates the generally accepted conclusions that the primary products of the reaction are carbon monoxide and hydrogen and that carbon dioxide is formed from the water-gas reaction which reaches or tends to reach equilibrium.

2. Available data suggest that the rate of gasification is governed by an adsorption isotherm for the steam and that a steam saturation pressure exists (its value depending on the carbon and the temperature), above which the rate of gasification at a given temperature becomes constant.

3. The nature of the intermediate adsorption complexes is discussed, the postulated reaction scheme being the following

(a) $C + H_2O \rightleftarrows C(H_2O)_{ads.} \rightleftarrows \underset{\text{formaldehyde}}{\underset{\text{adsorbed}}{(CH_2O)}} \rightleftarrows CO + H_2$

(b) $CO + H_2O \rightleftarrows (CO)_{ads.}(H_2O)_{ads} \rightleftarrows \underset{\text{formic acid}}{\underset{\text{adsorbed}}{(HCOOH)}} \rightleftarrows CO_2 + H_2$

4. A theory for the catalysis of the steam–carbon reaction is offered.

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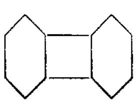
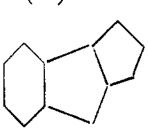
An Electron Diffraction Investigation of Biphenylene

BY JURG WASER AND VERNER SCHOMAKER

W. C. Lothrop[1] has synthesized an aromatic hydrocarbon $C_{12}H_8$ to which he assigns the structure (I) and the name biphenylene. It was thought worth while to establish the structure of Lothrop's biphenylene by other than chemical means. In this we have succeeded, mainly by the electron diffraction investigation described below. Our work confirms structure (I) and in particular rules out structure (II)


(I)


(II)

which has been proposed by W. Baker[2] and supported by C. A. Coulson.[3] Biphenylene and its derivatives synthesized by Lothrop are thus the first molecules of definitely established structure to contain the interesting aromatic four-ring. They should prove very valuable for studies of orientation effects due to conjugation and to strains of the bond angles (Mills–Nixon effect).

Our investigations were carried out with a 1.5-g. sample of the compound, kindly given to us by Dr. Lothrop.

Electron Diffraction Investigation

Procedure.—The electron diffraction investigation was feasible because of the relatively high vapor pressure of biphenylene. It was carried out with the use of the high temperature nozzle, which had to be heated to around 200°. The wave length of the electrons used, $\lambda = 0.0615$ Å. was determined by transmission pictures of gold foil ($a_0 = 4.070$ Å.). Of the sixty pictures which were taken at nozzle–film distances of about 10 or 20 cm., about a fifth showed satisfactory rings, some out to about $s = 25$ Å.$^{-1}$.

In principle, the problem of an electron diffrac-

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[1] W. C. Lothrop, THIS JOURNAL, **63**, 1187 (1941); **64**, 1698 (1942).

[2] W. Baker, *Nature*, **150**, 211 (1942).

[3] C. A. Coulson, *ibid.*, **150**, 577 (1942).

tion investigation by the visual method is the correlation of the observed features of the diffraction pattern with the corresponding features of an appropriate theoretical intensity function. In this study we have used functions of the form[4,5]

$$I'(s) = C \sum_{ij}{}' \frac{Z_i Z_j}{r_{ij}} \sin(s r_{ij})$$

in which $s = (4\pi/\lambda) \sin (\varphi/2)$, φ is the angle between direct and scattered beam, the r_{ij} are the interatomic distances and the Z_i are constants representing the scattering powers of the atoms.

From the appearance of the rings and their measured positions the visual curve (solid Z, Fig. 2) was drawn in accordance with our experience with the visual method to correspond to the general characteristics of curves of the type of $I'(s)$. (The position and height of the first peak were actually taken from the theoretical functions which were calculated after the rest of curve Z had been drawn.) The curve Z was used for the calculation of the radial distribution function described below and for a preliminary analysis of the theoretical scattering functions calculated for various models of the molecule. After this preliminary analysis the pictures were carefully reëxamined and directly compared with the calculated scattering curves. Modifications of the original curve Z, as suggested by this reëxamination, are indicated by dotted lines. For example it was found that features 6, 9 and 15 must correspond merely to small inflections of the curve.

The Radial Distribution Curve.—With the aid of the original visual curve (solid Z, Fig. 2) a radial distribution function

$$rD(r) = K \int \sin(sr) I'(s) \, ds$$

was obtained. This integral was approximated, with the introduction of a convergence factor $\exp.(-as^2)$, by a sum[5]

$$\Sigma \sin(s_i r) I'(s_i) e^{-as_i^2} \Delta s$$

taken in steps of $\Delta s = \pi/10$ out to $s = 27$. The value of a was chosen so that the exponential had the value 0.10 for the last term in the sum.

This radial distribution function R (Fig. 2) confirms the general structure (I) assigned to the compound by Lothrop. *E. g.*, the peak at 1.42 Å. corresponds to the average bonded C–C distance, while the peak at about 2.1 Å. corresponds to the diagonals of the four-ring and some C–H distances, and the peaks at 2.44 Å. (1.73 × 1.41) and at 2.78 Å. (2 × 1.39) represent the meta and para distances of the six-ring, respectively. The distance spectrum of model D (*cf.* Table I) is shown below the radial distribution curve R (Fig. 2). It is seen that the agreement continues to be satisfactory out to large distances. From a more detailed examination of the curve R one would expect an average six-ring C–C bond distance of 1.41 Å. Parameters e and α (Fig. 1) are interrelated in a somewhat complicated fashion; for α equal to 120° one finds e to be about 1.46 Å. If we examine now structure (II), proposed by Baker, we find its distance spectrum to be in complete disagreement with the curve R. Let us *e. g.*, take a model like P (Table I) as representative, consisting of a regular hexagon and two regular pentagons with a C–C bond distance of say 1.42 Å. The peak at 1.42 Å. is accounted for in this way, while the meta and para distances of the six-ring have perhaps not enough weight and the peak at 2.1 Å. is only accounted for by some C–H distances. Serious trouble however arises from the ten diagonals of the pentagons, having a length of 2.30 Å. The curve R has no peak at all near this distance. Any reasonable modification of this model would also give rise to pentagon diagonals centered around 2.30 Å. At larger distances the agreement is entirely unsatisfactory for model P and for modifications of this model. Structure (II) is therefore ruled out.

Theoretical Intensity Functions.—Theoretical scattering functions $I'(s)$ were calculated for

TABLE I

DISTANCES e AND ANGLES α FOR MODELS A TO J (ALL OTHER C–C BOND DISTANCES ARE 1.39 Å.)

e	119°	120°	121°	122°
1.39	A	C		
1.44	B	D		H
1.48			G	I
1.50		E		
1.52				J
1.54		F		

DISTANCES a TO e AND ANGLES α FOR MODELS K TO O

Model	a	b	c	d	e	α
K	1.41	1.38	1.41	1.41	1.45	118°
L	1.41	1.38	1.41	1.41	1.45	121°
M	1.41	1.38	1.41	1.41	1.45	124°
N	1.38	1.40	1.38	1.41	1.47	122°
O	1.38	1.40	1.38	1.41	1.47	124°

Model P consists of a regular hexagon and two regular pentagons with a C–C bond distance of 1.39 Å. The bonded C–H distances in all models are 1.08 Å. These models are all about 1.5% too small and the theoretical curves are shown in Fig. 2 with the corresponding change in scale.

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

(5) R. Spurr and V. Schomaker, THIS JOURNAL, **64**, 2693 (1942).

fifteen centrosymmetric, planar models with Lothrop's structure (Table I, curves A to O, Fig. 2), and for a single model representing Baker's structure (curve P, Fig. 2). The ratio of the scattering powers of carbon and hydrogen, Z_C/Z_H, was assumed to be five. In models A to J only the distance e and the angle α (Fig. 1) were varied, while a, b, c and d were kept at 1.39 Å.

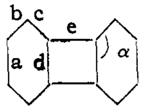

Fig. 1.

In models K to O the distances a, b, c and d were varied also; for models K to M the distances were taken from a simple valence bond treatment of the molecule,[6] while the distances of models N and O came from a molecular orbital treatment[7] (see below). Curve P was calculated for a regular hexagon and two regular pentagons with a C–C bond distance of 1.39 Å. The C–H bond distances were assumed for all models to be 1.08 Å. at directions bisecting the angles of the rings. (All of these distances were found to be somewhat too small and were finally increased by 1.5%; this has been accounted for in the final drawing of the intensity curves.)

The molecule was taken as rigid except for the C–H distances. For the bonded C–H terms the temperature factor exp($-bs^2$), b = 0.0022, was used. For the non-bonded C . . . H terms the effect of the appropriate temperature factor exp($-b's^2$), b' = 0.004, was obtained by plotting two curves for each model, the upper one out to $s = 17$ where $\exp(-b's^2) \approx 0.3$ including these terms, and the lower one beginning at $s = 8$ where $\exp(-b's^2) \approx 0.8$ omitting them. Out to about $s = 8$ the intensity function is well represented by the upper curve, from $s = 17$ on it is approximated by the lower curve, and in the intermediate region it is found by interpolation.

In the discussion of the resulting intensity curves (Fig. 2) all features except 2, 3 and 18 were helpful. Comparison between the calculated intensities and the pictures ruled out model P, as was to be expected from the disagreement of its distances with the radial distribution curve. No reasonable variation of the C–C distances of this model could possibly improve curve P, which looks so totally different from the visual curve Z.

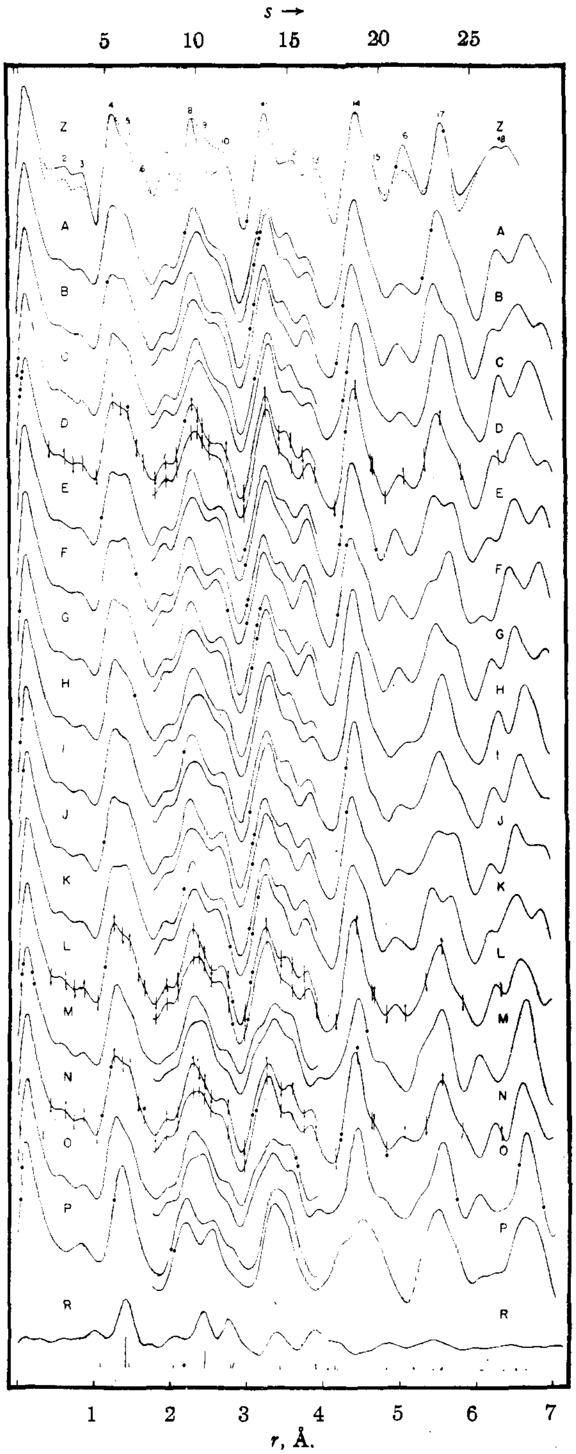

Fig. 2.

Of the models A to J, with equal ring C–C bond distances, A, C, D and I are about equally good. Models B, E, G and J are unsatisfactory and provide upper limits of the distance e for various choices of the angle α. Models M and O are

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[6] L. Pauling, "The Nature of the Chemical Bond," second edition, Cornell University Press, Ithaca, N. Y., 1940, p. 174.

[7] C. A. Coulson, *Proc. Roy. Soc.* (London), **A169**, 413 (1939).

TABLE II

AGREEMENT BETWEEN OBSERVED AND CALCULATED q VALUES, ($q = 15s/\pi$)

		Obs.	D		I		L		N	
Max.	Min.	q_0	q	q/q_0	q	q/q_0	q	q/q_0	q	q/q_0
4		25.3	25.9	1.024	26.1	1.032	25.9	1.024	25.9	1.024
	7	36.1	36.3	1.006	36.3	1.006	36.3	1.006	36.6	1.014
8		46.0	47.0	1.002	46.7	1.015	46.8	1.017	46.6	1.013
	11	59.5	59.9	1.007	59.6	1.002	59.4	0.998	59.6	1.002
11		65.1	66.8	1.026	66.9	1.028	66.5	1.022	66.9	1.028
	14	83.2	84.2	1.012	83.7	1.006	82.4	0.990	83.8	1.007
14		88.9	90.0	1.012	89.9	1.011	89.6	1.008	90.0	1.012
	16	96.5	98.4	1.020	98.9	1.025	97.9	1.015	99.0	1.026
16		101.3	102.1	1.008	102.4	1.011	100.6	0.993	102.6	1.013
Av.				1.015		1.015		1.008		1.015
a.d.				0.007		0.009		0.011		0.007

very unsatisfactory and serve to give an upper limit for α at 124°. (In these two models the ring C–C bond distances are not all alike.) Lower limits for the parameters e and α are not provided by our intensity curves, but a value for e smaller than the ring C–C bond distances can safely be ruled out on the basis of the same knowledge of molecular structure which prompted us to disregard non-planar and unsymmetrical models. Similarly a value of α smaller than say 118° is very improbable, as the strains in the molecule would tend to make α larger than 120° rather than smaller. As to models K to O, it is seen that L and N represent the scattering about equally well (N is perhaps somewhat better), although the ring C–C distances in the two models do show interesting differences. *E. g.*, b is the smallest ring distance in model L, while b and d are the largest ring distances in model N. On the basis of the present pictures it is therefore not possible to make any exact statements as to the different ring bond distances.

Table II gives the q values ($q = 15s/\pi$) for the nine most easily measured features and the values calculated from models D, I, L and N. The ratio q/q_0 and its average for each of these four models are also given. It is seen that the respective models have to be enlarged by 0.8 to 1.5%. The best agreement with all of them and with A and C is reached with the following choice of distances: average ring C–C bond distance = 1.41 ± 0.02 Å., bridge C–C distance e = 1.46 ± 0.05 Å., C–H distance = 1.10 Å. (assumed), angle α = 121° ± 3°.

Quantum Mechanical Calculations

If we assume that structure (I) is planar and centrosymmetric, we still are left with six parameters, *e. g.*, the five distances a to e and the angle α (Fig. 1). In order to provide a guide to the values which might be expected for these five distances, some quantum mechanical calculations were carried out.

The distances of models K, L and M were obtained by superimposing the five unexcited valence-bond structures of the molecule with equal weights.[5] From the double-bond characters thus found the distances were obtained by interpolation between the values 1.20 Å. for acetylene, 1.33 Å.[8] for ethylene, 1.39 Å.[8] for benzene, and 1.54 Å. for ethane. The resonance energy of structure (I) also was calculated by the valence bond method,[9] taking into account only the five unexcited structures with the result 2.093 α.[9] The resonance energy of the molecule which was found by the molecular orbital method[10] is 4.505 β.[11] The two results give a ratio of $\alpha/\beta = 2.22$, which agrees with the same ratio for benzene, provided the resonance energy between unexcited structures only is taken in the valence bond method. On the basis of the molecular orbital treatment the "bond order"[7] p of the various bonds was calculated with the result $p_a = 0.691$, $p_b = 0.621$, $p_c = 0.683$, $p_d = 0.565$, $p_e = 0.263$ (the ethylene double bond has $p = 1$, the single bond, $p = 0$). From these values the distances for models N and O were obtained by interpolation between the values for various C–C distances given above. In all these calculations no account was taken

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[8] W. S. Gallaway and E. F. Barker (*J. Chem. Phys.*, **10**, 88 (1942)) recently found the higher value of 1.35 Å. for the ethylene C–C bond. The correct value of the benzene C–C bond distance also may be somewhat higher than the one chosen here. For models K to O this may possibly account for the increase in size which was finally required.

[9] L. Pauling, *J. Chem. Phys.*, **1**, 280 (1933).

[10] L. Pauling and E. B. Wilson, "Introduction to Quantum Mechanics," McGraw-Hill Book Co., Inc., New York, N. Y., 1935, p. 381.

[11] The same value for the resonance energy was found by C. A. Coulson[5]

of the strain of the four-membered ring (*cf.* however Coulson, ref. 3).

Both sets of distances had to be increased somewhat to make the corresponding intensity curves agree more closely with the observed scattering. It is interesting to note that the two methods give even qualitatively different results for the various distances. If, however, we were to replace our somewhat coarse valence bond treatment by the more refined method of Penney[12] we would probably obtain the same results as we did using Coulson's method. The results of these two methods agree in all cases which have been carried through so far.

Discussion

As pointed out above, our investigations give conclusive evidence that biphenylene has the structure (I) proposed by Lothrop. It is, however, not possible at this stage to give precise values for all of the structural parameters. Average values only have been found for the ring distances, and the distance *e* between the two rings and the angle α (Fig. 1) have been fixed only within wide limits. It is therefore impossible to draw any very definite conclusions about such details of the electronic structure of the molecule as the double bond character of the bond *e* or the distribution of the strains of the bond angles.

In collaboration with Dr. Chia-Si Lu a crystal structure investigation of biphenylene is being carried out, and will be described in a later paper. The following preliminary results have been obtained. The monoclinic unit cell contains six molecules of biphenylene and the space group is very probably C_{2h}^5-$P2_1/a$. The general position in this space group is fourfold; in addition there are four twofold positions with the point symmetry C_i. Therefore, if we assume the above space group assignment to be correct, at least two of the molecules must have a center of symmetry. This makes highly improbable any structure of biphenylene which has no center of symmetry.

Because structure (II) is definitely eliminated by our investigations of both the vapor and the crystal, it seems worth while to discuss briefly the arguments given by Baker in favor of structure (II) and against structure (I). It is no doubt true that structure (I) is considerably more strained than structure (II) and probably less stable, as pointed out by Baker[2] and Coulson,[3] but it must be remembered that a reaction does not necessarily lead to the most stable of all possible products. Although cyclobutadiene has never been prepared, cyclobutane, cyclobutenes, cyclopropane and cyclopropene[13] have been prepared, showing that strain is no unsurmountable difficulty for the existence even of unsaturated four-rings or three-rings. Baker's catalytic reduction experiments resulted in the absorption of about three molecules of hydrogen per molecule of biphenylene. Since he expects a molecule of structure (I) to yield biphenyl upon catalytic hydrogenation, Baker used the above result as an argument for structure (II). But this result is as easily explained on the basis of structure (I) by the assumption that one of the six-rings becomes completely saturated without damage to the four-ring. Although a reliable prediction of the course of hydrogenation of biphenylene (structure (I)) could hardly have been made, the observed reduction of one of the six-rings in preference to a splitting of the four-ring is at least not surprising, inasmuch as hydrogenation of cyclobutene can be made to give cyclobutane rather than a straight chain butylene or butane and the hydrogenation of polynuclear aromatic hydrocarbons often stops at a stage such that the resulting molecule is partly aromatic and partly alicyclic (*e. g.*, naphthalene, anthracene, phenanthrene).

We are indebted to Dr. Linus Pauling for helpful discussion and criticism, and to Dr. W. C. Lothrop for the sample of biphenylene.

Summary

1. An electron diffraction investigation of biphenylene has been carried out, substantiating the formula (I) assigned to this compound by Lothrop and leading to the following distances and angles for the molecule (Fig. 1) average of *a*, *b*, *c*, *d* = 1.41 ± 0.02 Å., *e* = 1.46 ± 0.05 Å., C–H = 1.10 Å. (assumed), α = 121° ± 3°.

2. Quantum-mechanical calculations of the resonance energy and relative bond strengths in biphenylene have been made.

Pasadena, California Received March 26, 1943

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[12] W. G. Penney, *Proc. Roy. Soc.* (London), **A158**, 306 (1937).

[13] M. J. Schlatter, This Journal, **63**, 1733 (1941); Demjanow and Dojarenko, *Ber.*, **56**, 2200 (1923); *Bull. Acad. Sci. Russ.*, [6] 297 (1922).