nitrobenzotrifluoride[13] was added slowly and the temperature was controlled carefully so as not to exceed 100° for the first ninety minutes. Then the temperature was raised slowly and maintained at 115° for the next four to five hours. The entire reaction mixture was poured over crushed ice with rapid stirring, and the crude product separated as a white solid. It was removed on a large Buchner filter, washed with ice water, and dried. A yield of 43 g. or 52% was obtained. Recrystallization from methanol gave pure 3,5-dinitrobenzotrifluoride as white crystals, m. p. 49–50°.

Anal. Calcd. for $C_7H_3O_4N_2F_3$: C, 35.6; H, 1.28; N, 11.86. Found: C, 35.61; H, 1.25; N, 11.83.

3-Amino-5-nitrobenzotrifluoride (VIII).—To a refluxing solution of 47.2 g. of 3,5-dinitrobenzotrifluoride dissolved in 700 cc. of ethanol, 500 cc. of an alcoholic ammonium sulfide solution was added slowly over a period of thirty minutes, and refluxing was continued for approximately five hours. The ammonium sulfide[7] was prepared by treating 96 g. of crystalline sodium sulfide with 85.6 g. of ammonium chloride in ethanol, and removing the precipitated sodium chloride by filtration. After the reduction was complete, the reaction mixture was concentrated by evaporation to about 200 cc., cooled, filtered, and the precipitate of sulfur and inorganic salts was washed with ethanol to dissolve any residual nitroamine. The filtrate was poured into a large volume of water thus precipitating the nitroamine. After the crude product had been removed by filtration, it was extracted several times with hot, dilute hydrochloric acid. The acid extract was made alkaline and the nitroamine was isolated. A yield of 33 g. or 80% was obtained. Recrystallization from carbon tetrachloride gave pure 3-amino-5-nitrobenzotrifluoride as yellow flakes, m. p. 80–81.5°.

Anal. Calcd. for $C_7H_5O_2N_2F_3$: C, 40.78; H, 2.44; N, 13.59. Found: C, 40.87; H, 2.46; N, 13.48.

The acetyl derivative was recrystallized from carbon tetrachloride as white needles, m. p. 134–135°.

Anal. Calcd. for $C_9H_7O_3N_2F_3$: C, 43.53; H, 2.84; N, 11.29. Found: C, 43.69; H, 2.83; N, 11.20.

3-Fluoro-5-nitrobenzotrifluoride (IX).—This compound was prepared from 3-amino-5-nitrobenzotrifluoride by the Schiemann reaction. An 88% yield of the diazonium fluoborate was obtained. The thermal decomposition of the diazonium fluoborate gave a 43% yield of 3-fluoro-5-nitrobenzotrifluoride based on the amine. After purification the pure compound boiled at 180.5°.

Anal. Calcd. for $C_7H_3O_2NF_4$: C, 40.21; H, 1.45; N, 6.70. Found: C, 40.40; H, 1.44; N, 6.53.

3-Amino-5-fluorobenzotrifluoride (X).—This amine was prepared from 3-nitro-5-fluorobenzotrifluoride (IX) by the same general synthesis as indicated for IV. A 90% yield of crude 3-amino-5-fluorobenzotrifluoride was obtained. Recrystallization of the acetyl derivative from carbon tetrachloride gave white needles, m. p. 99.5–100.5°.

Anal. Calcd. for $C_9H_7ONF_4$: C, 48.88; H, 3.19; N, 6.33. Found: C, 49.11; H, 3.10; N, 6.57.

3,5-Difluorobenzotrifluoride (XI).—This compound was prepared from 3-amino-5-fluorobenzotrifluoride by the same general procedure as outlined under V. The yield of the diazonium fluoborate was 94%. Thermal decomposition of this compound gave 3,5-difluorobenzotrifluoride. The pure compound gave the following constants: f. p. *ca.* −40°, b. p. 94–95°, $n^{20}\text{D}$ 1.3873.

Anal. Calcd. for $C_7H_3F_5$: C, 46.17; H, 1.66. Found: C, 46.10; H, 1.53.

Summary

The preparation of 2,5- and 3,5-difluorobenzotrifluoride and some of their intermediates is described.

3,5-Dinitrobenzotrifluoride was prepared from 3-nitrobenzotrifluoride with a fuming nitric–sulfuric acid mixture.

URBANA, ILLINOIS RECEIVED JULY 17, 1944

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[13] Finger, Nachtrieb and Reed, *Trans. Illinois State Acad. Sci.*, **31**, 132 (1939).

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

The Structures of Biphenyl, *o*-Terphenyl and Tetraphenylene[1]

BY ISABELLA LUGOSKI KARLE[2] AND L. O. BROCKWAY

The nature of the binding between benzene rings which has been of considerable interest to the chemist has led us to investigate by electron diffraction the molecular structures of biphenyl, *o*-terphenyl and tetraphenylene (1,2,3,4,5,6,7,8-tetrabenz-$\Delta^{1,3,5,7}$-cyclooctatetraene). Although the original purpose of this investigation was to study the type of binding between aromatic groups, the problems of the orientation of the benzene rings in biphenyl and *o*-terphenyl and the structure of a substituted cyclooctatetraene ring presented themselves. The structures of biphenyl[3] and *o*-terphenyl[4] were studied previously by X-ray diffraction.

We wish to thank Dr. L. F. Fieser of Harvard University who forwarded to us a sample of tetraphenylene synthesized by Drs. W. S. Rapson and R. G. Shuttleworth of the University of Cape Town. This sample contained 10% benzene which was removed by placing the sample in the nozzle and heating it to 200° in a vacuum before electron diffraction photographs were taken. The *o*-terphenyl was supplied to us by Dr. W. E. Bachmann of the University of Michigan. It was recrystallized from petroleum ether according to the method of Allen and Pingert[5] and its m. p. was 58°. The biphenyl was obtained from the Eastman Kodak Co. and recrystallized from ethyl alcohol; m. p. 70°.

The electron diffraction photographs were obtained using a high temperature nozzle consisting of a monel metal cylinder closed by a screw cap in which a very tiny hole was bored. The cylinder

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[1] Taken from a dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Michigan. Original manuscript received December 13, 1943.

[2] Horace H. Rackham Fellow, 1943.

[3] Jagattaran Dhar, *Indian J. Physics*, **7**, 43–60 (1932).

[4] C. J. Birkett Clews and Kathleen Lonsdale, *Proc. Roy. Soc.* (London), **A161**, 493–504 (1937).

[5] Allen and Pingert, THIS JOURNAL, **64**, 1369 (1942).

was heated by means of a heater wire wound around it and a thermocouple was attached near the hole where the vapor escaped into the path of the beam. Eight to twelve photographs were taken of each compound at a camera distance of 10 cm. and an electron wave length of 0.0594 Å. Temperatures of 105, 145 and 200° were used for biphenyl, *o*-terphenyl and tetraphenylene, respectively.

The simplified theoretical intensity curves were calculated using the equation $I(s) = \sum_i \sum_j Z_i Z_j (\sin sr_{ij})/sr_{ij}$ where $s = 4\pi(\sin \theta/2)/\lambda$, r_{ij} represents the interatomic distances, and Z represents the atomic numbers.[6] Radial distribution curves were calculated using the Walter and Beach function[7]

$$r^2D(r) = K'r^2a_k \cos a_kr/(\pi^2 - 4a_k^2r^2) \sum_k s_k^2I(s_k) \sin s_kr/s_kr$$

Biphenyl.—The photographs were observed to have seven principal maxima. The second and sixth maxima are not symmetrical, showing a more gradual decrease toward the outside, and the third maximum is very sharp, whereas the fourth is broad with a shelf on the outer side which was easily measured. The fifth maximum has a shelf and a very weak maximum following it which was very difficult to measure. In models A, B and C (Fig. 1) the molecule was assumed to be coplanar with regular benzene rings. The C–C distance in the ring is 1.39 Å. in all three models and the C–C distance between the rings is 1.54, 1.48 and 1.44 Å., respectively. Qualitatively, curve A is in agreement with the photographs in all respects while curves B and C are unsatisfactory in that the pronounced shelf on the fourth peak is missing, the fifth peak has a wrong shape, and the sixth peak is too symmetric. A similar model, not illustrated, with a C–C distance between the rings of 1.58 Å. is quite unsatisfactory.

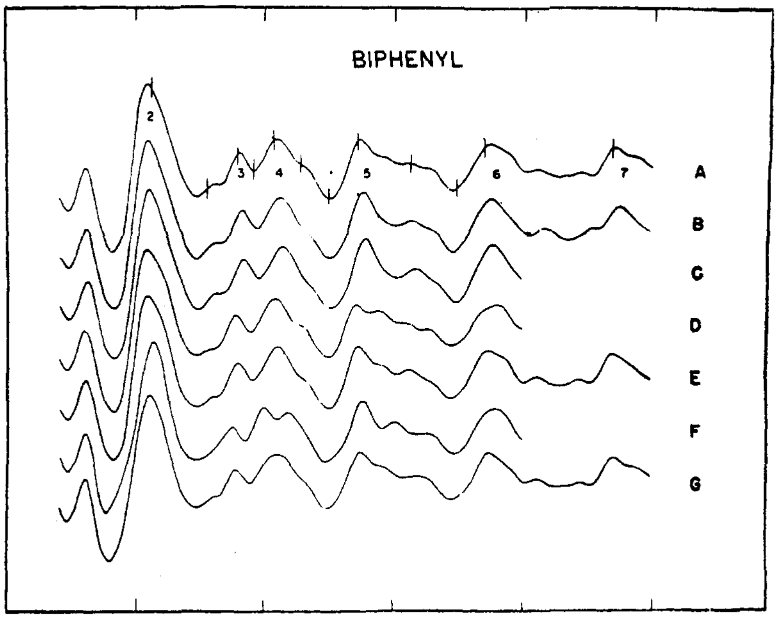
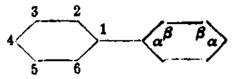


Fig. 1.

A distorted benzene ring is present in models D and E with the C_1–C_2 and C_3–C_4 distances equal to 1.40 Å., the C_2–C_3 distance equal to 1.38 Å., angle α equal to 117° and angle β equal to 121$^1/_2$°.



The distance between the rings is 1.54 and 1.48 Å., respectively, curve D is in disagreement with the observed pattern, but it is difficult to distinguish curve E from curve A except in the shape of the seventh peak which, however, was not too well defined on the photographs.

The possibility of non-coplanarity was investigated in models F and G. Model F is identical with model A except that the rings are orthogonal to one another. This model is quite unsatisfactory in that the shelf on the fourth peak developed into another peak. Free rotation of one ring with respect to the other was investigated by averaging curves for twenty-four equally spaced orientations of one ring with respect to the other. The result is curve G which is rather similar in appearance to curve A and quite acceptable.

Three different models (A, E and G) satisfy qualitatively the appearance of the photographs. No choice can be made from quantitative considerations (the s/s_0 ratios are given in Table I) since all three are equally good. The radial distribution curve (Fig. 2) also does not distinguish between these models. The values marked on the radial distribution curve are those for models A and G. The similarity of curves A and E means that the regularity of the benzene ring cannot be precisely determined. If the ring is made longer by deviating from 120° bond angles and the length of the molecule kept constant by shortening the inter-ring distance, no appreciable difference can be detected in the intensity curves. This situation especially limits the precision with which the inter-ring distance can be determined. However, if all angles are assumed to be 120°, then the inter-ring distance is 1.54 ± 0.03 Å., a value similar to the C–C distance found in ethane. The bonds in the rings are 1.39 ± 0.02 Å. Electron diffraction

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

(7) J. Walter and J. Y. Beach, *J. Chem. Phys.*, **8**, 601 (1940).

TABLE I

BIPHENYL

Max.	Min.	I_0	S_0	S_A/S_0	S_E/S_0	S_G/S_0
2		20	5.61	0.970	0.971	0.986
	2	− 8	7.73	(.948)	(.951)	(.946)
3		8	8.92	1.012	1.004	1.000
	3	− 5	9.59	1.000	0.999	0.990
4		8	10.34	1.013	1.018	1.018
Shelf		2	11.38			
	4	−12	12.46	1.003	1.003	0.998
5		9	13.61	1.005	1.004	1.008
	5	− 6	17.42	0.992	0.990	0.991
6		5	18.52	1.010	1.008	1.010
7		3	23.53	1.005	1.005	1.005
	Average			1.001	1.000	1.001
	Average deviation			0.009	0.009	0.009

data alone cannot answer the question of coplanarity.

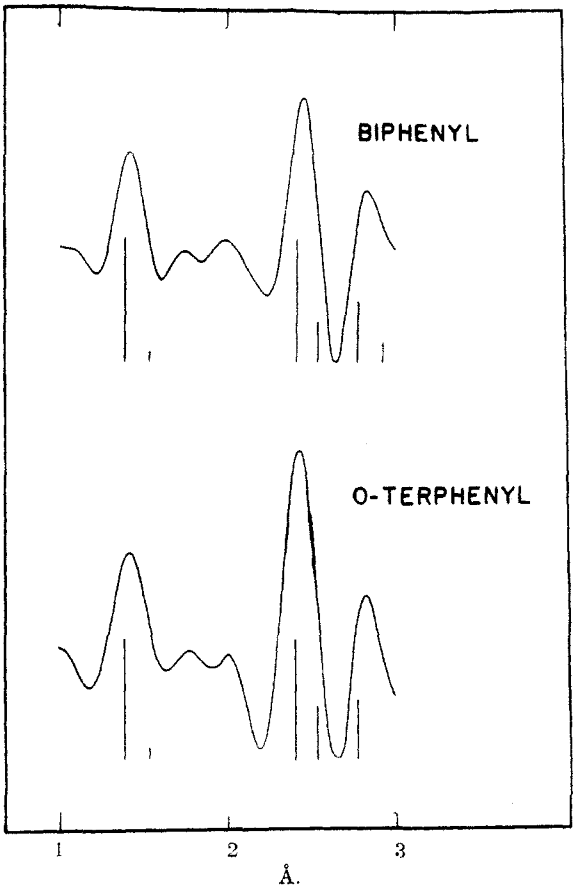

Fig. 2.

The X-ray determination of the crystal structure of biphenyl[3] led to a value of 1.48 Å. for the inter-ring distance and of 1.42 Å. for the ring bonds. These values differ from those reported above as a result of the electron diffraction investigation (1.54 Å. and 1.39 Å., respectively), but it is very probable that the agreement between calculated and observed X-ray intensities would not be affected by decreasing the benzene ring size to 1.39 Å. without shifting the position of the ring centers. Only coplanar models were considered. The assumption of coplanarity was based upon the fact that the biphenyl crystal belongs to the C_{2h}^5 space group and that with two molecules in a unit cell each molecule must have a center of symmetry; and also upon the fact that Smyth[8] showed zero dipole moments for *p*,*p*′-dichloro- and *p*,*p*′-dinitrobiphenyl. The zero dipole moments do not in fact have any bearing on the question of coplanarity, and they were correctly interpreted by Smyth to mean that the 1,1′,4 and 4′ carbon atoms lie on a straight line, with the orientation of the rings about the line joining the 4 and 4′ positions remaining indeterminate. If the space group is correctly assigned in the X-ray examination, however, the molecule must be coplanar, although a consideration of the distance between the ortho hydrogen atoms makes this seem improbable.

A separation of the ortho hydrogen atoms in biphenyl in a coplanar configuration is 1.84 Å., assuming 120° bond angles and 1.09 Å. for the C–H distance. The nearest approach of hydrogen atoms in different molecules in such crystals as methane,[9] hexamethylbenzene[10] and durene,[11] is 2.0 Å. Hydrogen atoms in the same molecule may be closer together if the energy gained by the particular configuration is greater than the repulsions due to the close approach of the hydrogen atoms, but it is doubtful that this is the case in a coplanar configuration of biphenyl. In 1,3,5-triphenylbenzene, for example, the bonded rings are not coplanar as shown by the X-ray examination and the study of the magnetic anisotropy made by K. Lonsdale,[12] but the three surrounding rings are each rotated about 25° out of the plane of the center ring in a propeller-like fashion. The interferences between the ortho hydrogens on adjacent rings are the same as in biphenyl, and one would expect these interferences to produce similar distortions in biphenyl.

Some further evidence on the configuration of phenyl groups about a common bond is afforded by the investigation of stereoisomerism in compounds such as the *m*,*m*′-disubstituted biphenyls. The failure of the many attempts to isolate geometric isomers indicates that these molecules are not rigidly coplanar. While the negative results in the attempts to isolate isomers do not support any particular equilibrium configuration, they do indicate that the coplaner configuration cannot be appreciably more stable than any other. Hampson and Weissberger[13] conclude from a study of

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(8) Charles P. Smyth, *Ind. Eng. Chem.*, **23**, 1224 (1931).

(9) Mooy, *Proc. Koninkl. Akad. Wetenschappen Amsterdam*, **34**, 550 (1931).

(10) L. O. Brockway and J. Monteath Robertson, *J. Chem. Soc.*, 1324–1332 (1939).

(11) J. Monteath Robertson, *Science Progress*, **33**, 666–670 (1939).

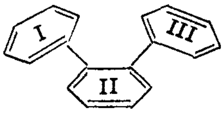
(12) K. Lonsdale, *Z. Krist.*, **A97**, 91 (1937).

(13) G. C. Hampson and A. Weissberger, THIS JOURNAL, **58**, 21[illegible] (1936).

the dipole moment and of the relative potential energies of the *cis* and *trans* configurations of *m,m'*-dichlorobiphenyl that the rings in this compound have virtually free rotation.

We conclude that a non-coplanar structure for biphenyl is more probable because it avoids the steric hindrance between the ortho hydrogen atoms in the planar structure and because it is compatible with the electron diffraction data.

***o*-Terphenyl.**—The molecule of *o*-terphenyl cannot be planar since the distance between the closest pair of non-bonded carbon atoms in a planar model can be at most 1.6 Å., which does not allow enough space for the van der Waals radius for carbon. An X-ray examination of the crystal structure of this molecule indicated that rings I and III are rotated both in the same direction about 45° out of the plane.[4] Two curves for such a model were calculated using 1.39 Å. in the benzene rings and 1.48 and 1.54 Å. between the rings. Curve A represents the latter model (Fig. 3). It is unsatisfactory in the region of the fourth maximum where a doublet should appear instead of a single maximum and in the region of the fifth maximum where there should be a rather strong peak followed by two weaker peaks. Accordingly other orientations of the rings were tried.



Models B, C and D involve the same distances as model A; however, rings I and III are orthogonal to ring II in model B, rings I and III are rotated in opposite directions 75° out of the plane in model C, and rotated in the same direction in model D. The value of 75° was chosen in order to make the distance between the nearest hydrogen atoms at least 2.0 Å. Although all three curves are acceptable, curve B is somewhat preferable since some observed structure in the second and fourth minima is missing in the latter two curves.

To observe the effect of changing the distance between the rings curves E and F were calculated using 1.48 and 1.60 Å. between the rings, otherwise they are the same as curve B. Qualitatively curve E is just as good as curve B, but curve F is not satisfactory in the region of the fifth maximum since there should be a strong peak followed by two weak ones. Table II shows the quantitative agreement between the observed values of *s* and those obtained from curves B and E. Precise determination of the distance between the rings and the regularity of the benzene ring cannot be made as was demonstrated in the determination of biphenyl. The inter-ring distance is probably in the vicinity of 1.52 Å. This is in agreement with the results obtained from the radial distribution curve (Fig. 2). The curve was calculated only up to 3.00 Å. since after that value the distances have too small coefficients to be of importance.

TABLE II

o-TERPHENYL

Max.	Min.	I_0	S_0	S_B/S_0	S_E/S_0
2		20	5.60	1.014	1.021
	2	−8	7.25		
3		8	8.84	0.998	1.008
	3	−6	9.43	0.989	1.003
4		6	10.07	0.996	1.007
	4	−1	10.52	1.009	1.020
4a		4	10.99	1.009	1.003
	4a	−10	12.57		
5		9	13.62	1.014	1.023
	5	−2	14.48	1.001	1.013
5a		2	14.96	1.008	1.022
	5a	−1	15.52	1.017	1.026
5b		2	16.31	0.996	0.998
	5b	−4	17.47	0.990	0.986
6		4	18.64	1.008	1.005
	Average			1.004	1.010
	Average deviation			0.008	0.010

Although curves B and E satisfy the experimental data for the structure of *o*-terphenyl best, it must be realized that an orientation of rings I and III such that they are orthogonal to ring II is probably an average position. Since curves C and D are within the limits of acceptability, and since there is no detectable difference between them even though in one case rings I and III are rotated in the same direction and in the other case they are rotated in opposite directions, rings I and III may be free to oscillate independently of one another through an angle of about 30°, where the average position is normal to ring II. It is improbable that the rings oscillate more than about 15° from the normal position since the minimum between the doublet of the fourth feature is very small in curve C and would disappear in curves of

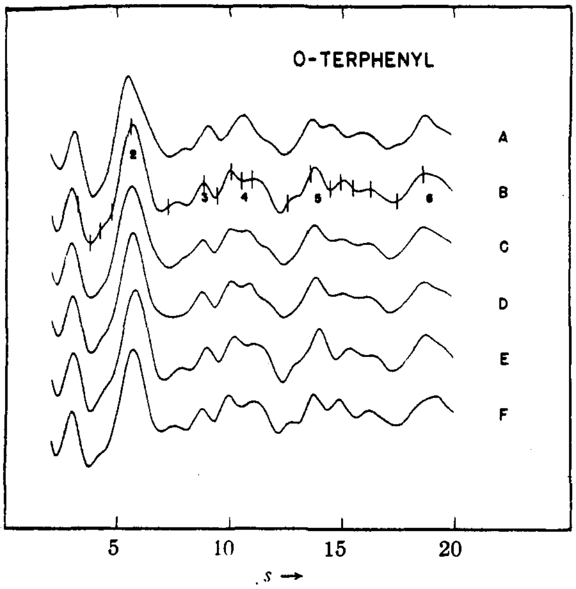


Fig. 3.

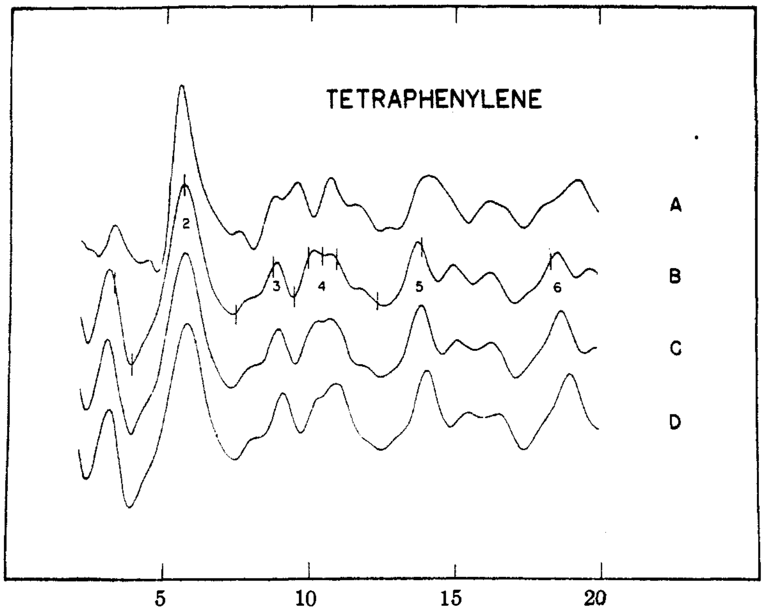
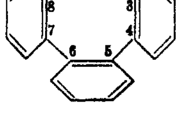


Fig. 4.

models with rings rotated through larger angles from the normal as is apparent in the 45° case (curve A). The best model for *o*-terphenyl has a C–C distance in the benzene ring of 1.39 ± 0.02 Å. and an inter-ring distance of 1.52 ± 0.04 Å.

Attempts were made to obtain electron diffraction photographs of *p*-terphenyl. When the sample was heated in the vacuum the vapors condensed on the walls of the apparatus. The *p*-terphenyl fluoresced when it came into contact with the electron beam and the light produced darkened the photographic plates so that the diffraction pattern was not discernible.

Tetraphenylene.—Two serious difficulties are encountered if a planar model of tetraphenylene is assumed with regular benzene rings and four-fold symmetry. The hydrogen atoms in the ortho positions on adjacent benzene rings have a distance of less then 1.0 Å. between their centers. Since these hydrogen atoms are on different benzene rings, a much larger separation is expected. The other difficulty is that a planar octagon must have angles of 135°. Previous studies on such molecules as hexamethylbenzene[14] and naphthalene[15] have shown that the three bonds on a carbon atom in an aromatic molecule tend to be coplanar with 120° angles. Thus a planar octagon in this molecule introduces strain in the bonds of the aromatic carbon atom.



Intensity curves for four planar models with regular benzene rings having a C–C distance in the ring of 1.39 Å. and a C–C distance between the rings ranging from 1.43 to 1.58 Å. are very similar qualitatively and all prove unsatisfactory. Curve A (Fig. 4) represents one of these models with a distance of 1.54 Å. between the benzene rings. Since the observed pattern of the photographs is represented quite well by curve B, it is seen that curve A is in definite disagreement with the observed pattern in the number, shape, and position of the maxima.

A different type of model incorporating all the structural features ascribed to aromatic hydrocarbons was tried next. All four benzene rings are regular and planar, the three bonds from each carbon atom in the octagon are in a plane, and in particular 120° bond angles exist between every pair of bonds. The octagon is staggered in pairs of atoms so that two opposite pairs of atoms are in one plane with the remaining two pairs in a parallel plane. The benzene rings of which the atoms in the octagon are a part are so arranged that the lines joining the centers of the rings outline a regular tetrahedron. Fig. 5 is a photograph of this model.

Curves B, C and D are based on the model just described with a C–C distance in the benzene ring of 1.39 Å. and a C–C distance between the rings of 1.54, 1.48 and 1.39 Å., respectively. The C–H distance was assumed to be 1.09 Å. in all cases. Curve B agrees very well both qualitatively and quantitatively (Table III). Curve C can be accepted as a lower limit with respect to the distance between the benzene rings since the intensities of the doublet (feature 4) have been reversed. Curve

TABLE III

TETRAPHENYLENE

Max.	Min.	I_0	S_0	S_B/S_0	S_C/S_0
2		20	5.62	0.993	1.004
	2	−10	7.42	0.980	0.984
3		8	8.80	1.010	1.013
	3	− 5	9.43	0.994	1.009
4		5	9.93	1.013	1.036
	4	− 1	10.40	1.004	1.004
4a		4	10.90	0.977	0.982
	4a	−10	12.30	1.018	1.013
5		6	13.84	0.990	1.001
6		3	18.30	1.013	1.022
	Average			0.999	1.007
	Average deviation			0.012	0.012

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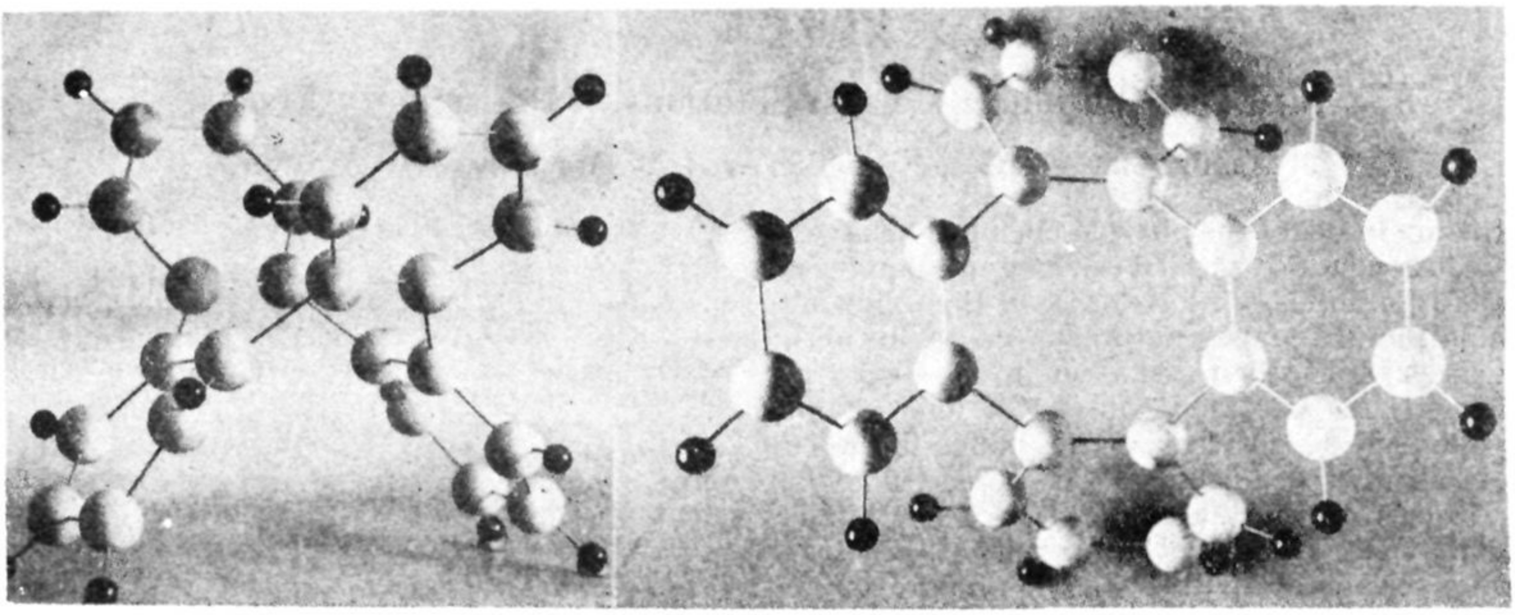
[14] K. Lonsdale, *Proc. Roy. Soc.* (London), **A123**, 494 (1929).

[15] J. Monteath Robertson, *ibid.*, **A140**, 79 (1933).

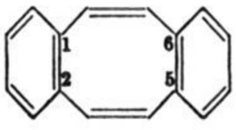


(a) (b)

Fig. 5.—Model of tetraphenylene: (a) view in average plane of eight-membered ring; (b) view along axis normal to eight-membered ring.

D with equal distances in the octagon is unsatisfactory especially in the region of the doublet. No information can be obtained from a radial distribution curve since there are too many distances in the molecule and too few measurements of s_0 values to obtain good resolution.

Since the number of parameters in the molecule is large and an exact solution is impossible, the regularity of the benzene ring and small deviations from 120° bond angles were not investigated. The excellent agreement between the complicated pattern of the photographs and curve B, however, leads us to believe that the structure is very close to model B. It is significant that the centers of the four 6-membered rings lie at the corners of a regular tetrahedron and that the 8-membered ring is not coplanar and does not have equal distances. Thus it is shown that the structure of a substituted cyclooctatetraene ring is not analogous to the structure of benzene. This is confirmed by the fact that the eight-membered ring in 1,2,5,6-dibenzcyclooctatetraene



is readily brominated[16] showing an unsaturation analogous to that of ethylene, not that of benzene. The final values for the parameters in the molecule are that the C_1'–C_2' distance is 1.39 ± 0.02 Å., that the C_2–C_3 distance is 1.52 ± 0.04 Å., and that all the C–C–C angles are near 120°.

The molecular structure of biphenylene was investigated recently by electron diffraction by J. Waser and V. Schomaker.[17] The C–C in the benzene ring was reported to be 1.41 ± 0.02 Å. while the inter-ring distance was 1.46 ± 0.05 Å.

The assistance of the Horace H. Rackham Foundation and of the Midgley Foundation in providing equipment is gratefully acknowledged.

Summary

The molecular structures of biphenyl, o-terphenyl and tetraphenylene were studied by electron diffraction. The non-coplanarity of tetraphenylene and o-terphenyl was established and the possibility for the non-coplanarity of biphenyl was discussed. In o-terphenyl the average position of the two attached rings is orthogonal to the central ring with possible oscillations of 15° from the normal position. On the other hand, in biphenyl much larger oscillations from the normal position probably occur.

The cyclooctatetraene ring is non-planar with bonds alternating in length around the ring, the shorter bonds being common to the six-membered rings. The benzene rings are directed alternately above and below the average plane of the molecule in such a way that the external bonds form 120° angles with the rings. This structure indicates that the substituted cyclooctatetraene ring is not conjugated in the way that cyclohexatriene (benzene) is.

The average bond distances in the aromatic rings of all three compounds are 1.39 ± 0.02 Å., although small deviations about this value due to irregularities in the rings would not have been detected. If the rings are regular, the distance between them is 1.52 ± 0.04 Å., as compared with the value 1.48 Å. reported in early X-ray determinations of conjugated aromatic rings. The conjugation effect on the inter-ring distances is probably small, although the distance may be appreciably less than 1.52 Å. if the rings are irregular. The non-coplanarity of the several molecules supports the probability of small conjugation effects.

ANN ARBOR, MICH. RECEIVED AUGUST 28, 1944

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(16) Private communication from L. F. Fieser and M. Pechet (see Abstracts, Detroit Meeting of the American Chemical Society).

(17) J. Waser and V. Schomaker, THIS JOURNAL, 65, 1451 (1943).