almost immediately; after recrystallization from aqueous alcohol, the yield of (III) was 104 g. (84%), m. p. 259° d. (lit.[3] m. p. 257°), entirely stable when heated with water at 100° (compare ref. 3).

Anal. Calcd. for $C_8H_{18}IN$: C, 37.96; H, 6.36; N, 5.53. Found: C, 38.33; H, 6.60; N, 5.57.

The same methiodide (III) was obtained when the mixed bases (II) were methylated according to directions[1] in the literature. As a characteristic derivative, the picrate was prepared from concentrated aqueous solutions of (III) and of sodium picrate, needles from ethanol, m. p. 112.5–113.0°.

(III) was not amenable to catalytic reduction; it was converted to the corresponding chloride[3] which was hydrogenated in aqueous solution under two atmospheres pressure using a palladium–charcoal catalyst. Two moles of hydrogen was taken up; the product was characterized by conversion to the picrate, prisms, m. p. 93.2–94.0°, from ethanol–isopropyl ether, and to the bromide, needles, m. p. 181.0–181.5°,[11] from ethanol. These derivatives gave no depression when mixed with authentic samples of the corresponding *n*-amyltrimethylammonium salts made from *n*-amyl bromide and trimethylamine.

Pirylene (IV)[1].—Quaternary iodide (III) (57.5 g.) was introduced together with 27 g. of potassium hydroxide and 70 cc. of water into a flask, and the mixture distilled from an oil-bath into a receiver immersed in a bath at −15°. A smooth decomposition took place (bath temperature 120–135°); the distillate was acidified with 6 *N* hydrochloric acid, and the hydrocarbon separated and dried over potassium carbonate, and over sodium. After distillation through a precision column, 8.9 g. (59%) of (IV) was obtained which boiled constantly; in

a second similar experiment the yield was 11.0 g. (73%) of material having a 0.3° range. The constants observed were: b. p. 59.4° at 744 mm., d^{25}_4 0.7339, n^{25}D 1.4467 (lit. pirylene[3]: b. p. 60°, d^{19}_4 0.7443, n^{19}D 1.4505; methylvinylacetylene (V)[7]: b. p. 59.2° at 760 mm., d^{20}_4 0.7401, n^{20}D 1.4496); the material polymerized slowly (much less rapidly than (VI)) on standing (compare refs. 3, 7).

The hydrocarbon (IV) (2.140 g.) was hydrogenated in ethanol solution using a palladium–charcoal catalyst. The hydrogen adsorbed (2.415 l. at 23° and 745 mm.) corresponded to 3 double bonds. The reduced hydrocarbon was distilled from the reduction mixture, treated with concentrated sulfuric acid and redistilled through a precision column; the sole product detected was *n*-pentane, yield 1.0 g., b. p. 36.3–36.5° (lit.[12] 36.1°).

Methylchloroprene (VI) was prepared from 3.7 g. of (IV) according to directions in the literature.[8] Two and two-tenths grams of (VI) b. p. 98.5–101°, n^{25}D 1.4745 (lit.[8] b. p. 99.5–101.5°, n^{20}D 1.4785) was obtained, and 1.5 g. of hydrocarbon was recovered. (VI) was identified by condensing with α-naphthoquinone; the derivative[8] melted at 180.7–181.0° cor. (lit.[8] 181°). When excess of (IV) and α-naphthoquinone were heated for two hours in a sealed tube at 100° no reaction[13] was observed.

Summary

The conclusion, first arrived at as a result of the electron diffraction investigation,[6] that pirylene and 1-methyl-2-vinylacetylene are identical, is supported by the chemical evidence.

(12) Egloff, "Physical Constants of Hydrocarbons," Vol. I, Reinhold Publishing Corp., New York, N. Y., 1939, p. 33.

(13) Compare Butz and Joshel, THIS JOURNAL, **63**, 3344 (1941). Under the same conditions, piperylene gave an adduct which was oxidized to 1-methylanthraquinone, m. p. 170–171°.

PASADENA, CALIF.   RECEIVED JULY 7, 1942

(11) von Braun and Murjahn, *Ber.*, **59**, 1205 (1926), reported the m. p. 175–176°.

The Constitution of Pirylene: Electron Diffraction Investigation

BY ROBERT SPURR AND VERNER SCHOMAKER

In connection with the studies described in the foregoing article[1] we have carried out an electron diffraction investigation of the C_5H_6 hydrocarbon pirylene with the object of determining its structural formula. Our results show that pirylene does not contain a three or four-membered ring as suggested by von Braun and Teuffert[2] but that it is methylvinylacetylene, $CH_3—C{\equiv}C—CH{=}CH_2$. This identification is substantiated by the agreement[1] of the physical properties of pirylene with those reported for methylvinylacetylene and by chemical evidence.[1] We wish to express our thanks

to Dr. E. R. Buchman for suggesting the problem and to him and his collaborators for providing the sample of pirylene used in the investigation.

Experimental

The preparation of the pirylene has been described.[1] The apparatus and technique used have been reviewed by Brockway.[3] Twenty photographs were taken of the scattering from the vapor. The camera distance was about eleven or about twenty centimeters, and the wave length of the electrons was about 0.06 Å. (based on $a_0 = 4.070$ Å. for Au). The diffraction pattern showed fine structure indicative of long inter-

(1) Herbert Sargent, Edwin R. Buchman and John P. Farquhar, THIS JOURNAL, **64**, 2692 (1942).

(2) von Braun and Teuffert, *Ber.*, **61**, 1092 (1928).

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

atomic distances of the order of 5 Å. Thirty-one features were measured; the q values are represented by the arrows drawn through curves E' and E $q = \frac{40}{\lambda} \sin \frac{\psi}{2} = \frac{10}{\pi} s$, where λ is the electron wave length and ψ is the scattering angle). The intensity pattern is well represented by curve E' in the figure for $q < 40$ and by curve E for $q > 40$.

Discussion

In most electron diffraction investigations the structural formula of the compound is known and the task is to find certain interatomic distances and bond angles. In the case of pirylene, however, only the molecular formula was known, and it was desired to find the correct structural formula (there are about 30 possibilities) even though a precise determination of the various important parameters seemed not to be feasible. To do this the expected molecular structures corresponding to the various structural formulas were compared with the information obtainable from the electron diffraction photographs with the aim of finding the satisfactory formula and eliminating all the others.[4] The procedure followed involved mainly the use of the radial distribution function[3] together with only a few theoretical intensity curves, as described below.

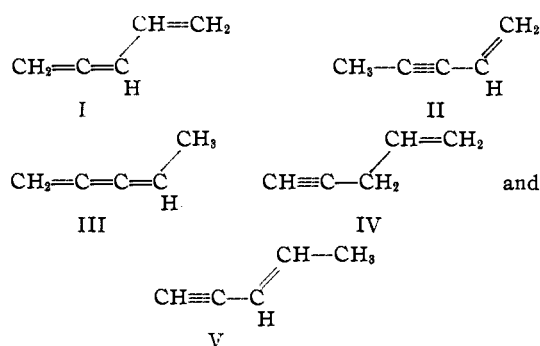The radial distribution curve R is a plot of

$$r\mathrm{D}(r) = \sum_{n=0}^{88} I_n e^{-n n^2} \sin \frac{\pi}{10} r n \qquad (e^{-n(88)^2} = 0.1)$$

where the I_n are the ordinates at unit intervals of q of a curve drawn to represent the appearance of diffraction pattern, the measured positions of the rings, and the general characteristics of the simplified theoretical intensity function as defined below. With this interval of q, this radial distribution summation is still an entirely satisfactory approximation to the corresponding Fourier integral for $r = 5$ Å., and no false peaks of significant size are to be expected (except from possible errors in the I_n) for values of r less than about 10 Å. We have found that radial distribution summations of this kind are superior to the ordinary summations especially at large values of r, where the heights of the peaks of the ordi-

nary summations are difficult to interpret and false peaks often appear. With these exceptions, the ordinary summations made for pirylene agreed well with R.

Since the radial distribution curve shows that there are important interatomic distances in the molecule up to about 5 Å., and none greater (the longest carbon–carbon distances expected for structures containing a ring or a branched chain is about 4.2 Å.), and since no branched chain or ring structures giving good general agreement with the radial distribution function could be found, an extended structure is indicated. Of the extended structures, only I and II will be

given detailed consideration here. It was found that the interatomic distances expected for structures III, IV, and V are in disagreement with the radial distribution curve, and that theoretical intensity curves (not shown here) drawn for models representing these structures bear little resemblance to the observed diffraction pattern; moreover, these structures are unlikely for chemical reasons.[5]

The intensity curves of Fig. 1 were drawn[6] for

(5) Structures IV and V may be definitely excluded because pirylene does not undergo the typical reactions of substances which contain an acetylenic hydrogen atom. See Ladenburg, Ber., 15, 1024 (1882); Ann., 247, 56 (1888), and the procedure for the preparation of pirylene, ref. 1.

(6) The intensity functions were calculated according to the formula

$$I = \sum_{ij}{}' \frac{Z_i Z_j}{r_{ij}} e^{-a_{ij} q^2} \sin \frac{(\pi q r_{ij})}{10}$$

with the use of International Business Machines. In the temperature factor the coefficients a_{ij} were taken as zero for all except the C—H bonded interactions, for which the value 0.00022 was used. The non-bonded C...H terms, which require a more severe temperature factor, were omitted except for the best model, E. For it the intensity function E was calculated with the omission of these terms, and the function E' with their inclusion with a_{ij} equal to zero. The probable effect of these terms was estimated for the other models by a comparison of E and E'. In the correlation of Model E with the measured q values a transition from curve E' to curve E was made in the region where a_{ij} values of 0.00044 would reduce the non-bonded C...H terms to approximately one-half their initial amplitude. In the figure the arrows representing the measurements change from E' to E at this point. The C—H distance was taken

(4) Since the present knowledge of the bond distances and bond angles in the lower hydrocarbons is very extensive (see L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, N. Y.; L. Pauling, H. Springall, and K. Palmer, THIS JOURNAL, 61, 927 (1939)), the predictions made for pirylene are almost certainly sufficiently accurate for this choice of the structural formula, and the reliability of the choice will depend only on the accuracy and completeness of the electron diffraction data.

the models shown below with the indicated distances and angles. All of the models are coplanar with respect to the carbon atoms; it is to be noted that A has the *trans* or extended configuration.

CH=CH₂ ... (structures A and B diagram)

A   B

CH₂   CH₂

C   D

CH₂

E
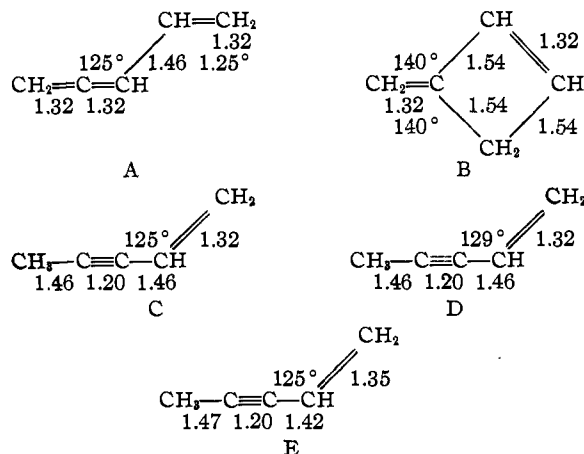
These models represent the remaining possible structures, I (model A) and II (C, D, and E;

<div>

TABLE I

Max.	Min.	$q_{calcd.}$[a]	$q_{obsd.}$	$q_{calcd.}/q_{obsd.}$
	2		3.18	
2			4.70	
	3		6.56	
3			8.73	
	4		11.05	
4			12.52	
	5	13.5	13.98	0.966
5		18.4	17.91	1.027
	6		19.06	
6			20.27	
	7		21.67	
7			23.76	
	8	27.2	27.27	0.997
8		32.0	31.40	1.019
	9		32.95	
9			35.42	
	10	37.5	36.78	1.020
10		40.5	40.07	1.011
	11	43.0	42.69	1.007
11		45.7	45.93	0.995
	12		47.23	
12			48.39	
	13		52.71	
13		57.5	56.46	1.018
	14	59.0	58.10	1.015
14		60.5	60.31	1.005
	15		64.72	
15		69.8	68.72	1.016
	16	71.5	71.41	1.001
16		74.5	74.18	1.002
	17		78.51	
17		85.0	85.31	0.996
	Average			1.006
	Average deviation			0.011

[a] Only the more easily measurable features are chosen for comparison with calculated q values.

</div>

the parameters of C and D include small variations from the expected values used in E), and the ring structure most favored by von Braun and Teuffert.[2,7]
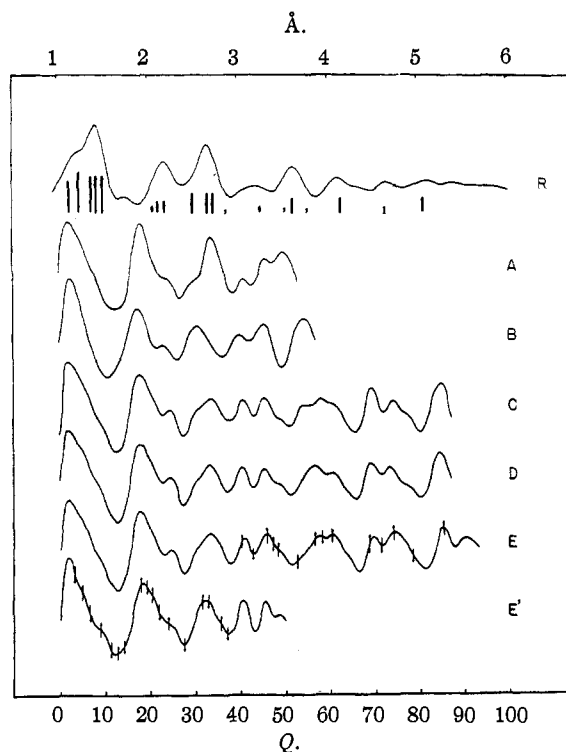

Fig. 1.

The appearance of the pictures is well represented only by curves E' and E, although for $q < 50$ C and D are not significantly less satisfactory than E. The numerical comparison for E'-E,[6] given in the table, possesses satisfactory internal consistency and indicates that the over-all size of the model is essentially correct. The agreement between the radial distribution function and the interatomic distances of model E is

as 1.09 Å., the bond angles involving hydrogen were based on ethylene and methane, and for hydrogen Z was replaced by the value 1.25.

The use of the intensity function here described, which differs from the one usually used[3] by the factor q, will be discussed in detail at a later time; it offers advantages of convenience both in the construction of the radial distribution function and in the correlation procedure. Only at small values of q does the difference in behavior of the two functions become great. There, however, the measured ring diameters are not sufficiently reliable for use in the quantitative comparison anyway, and neither function faithfully represents the appearance of the photographs although either can be used to the extent that experience and comparison with molecules of known structure can be used as guides.

(7) The bond angles involving the side chain in this model were given a value (140°) larger than expected in an effort to obtain better agreement with the radial distribution function.

very satisfactory as shown by the vertical lines under the peaks in the figure.

The other intensity curves are quite unsatisfactory. Curve B is of some interest because it lacks the fine structure on the inside of the first minimum which appears on the other curves, apparently as a result of the terms above 4 Å. The possibility of obtaining a satisfactory curve with any reasonable variation of Model A seems remote. One cause of the disagreement with Curve A is revealed by the width and position (1.42 Å.) of the first peak of the radial distribution function. For Model A one would expect instead a rather sharp peak at about 1.34 Å. with weak shoulders or satellites at 1.46 Å. and 1.09 Å. Another factor is the absence of any distance which would correspond to the radial distribution peak at 4.12 Å.

Our electron diffraction investigation thus leads to the conclusion that pirylene is 1-methyl-2-vinylacetylene (Structure II) with the bond distances and bond angles which were assumed for Model E from the existing information regarding similar molecules. Because the agreement of the photographs and the radial distribution function with Model E is so detailed that it could hardly be fortuitous, we should have confidence in this conclusion even if no effort to eliminate other possible formulas had been made.

Summary

The electron diffraction investigation of pirylene shows it to be 1-methyl-2-vinylacetylene. The structural parameters found were those anticipated from a knowledge of the structures of similar molecules.

An approximation to the radial distribution integral which is more accurate than the usual summation is briefly described.

Cyclobutane Derivatives. I.[1] The Degradation of cis- and trans-1,2-Cyclobutanedicarboxylic Acids to the Corresponding Diamines

By Edwin R. Buchman, Alf O. Reims, Thurston Skei and Maurice J. Schlatter

According to scattered references in the literature,[2] the Curtius degradation of cyclic dicarboxylic acids proceeds in the normal fashion without change in configuration. In the present work it was found that the cis- and trans-isomers (III) could be converted, over the intermediates (IV) and (V), into the corresponding diaminocyclobutanes (VI). The diamine obtained from the cis-acid was shown to possess the cis-structure by the preparation from it of cyclic derivatives; under the same conditions cyclic products were not obtained from trans-(VI).

The K. F. Schmidt degradation[4] had not previously been applied to cyclic dicarboxylic acids. When cis- and trans-(III) were treated with
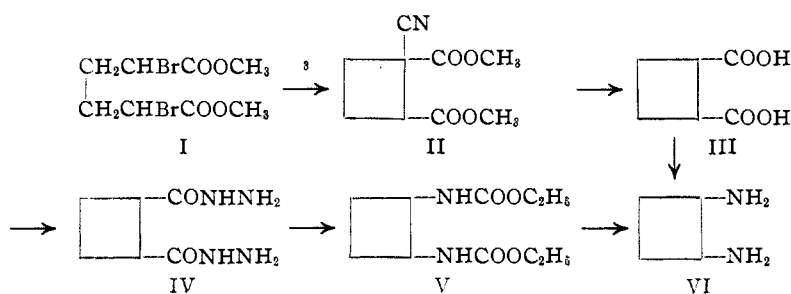
hydrazoic acid according to this method they were transformed directly, with retention of configuration, to cis- and trans-(VI); thus the method affords an alternative preparative route to these substances.

(1) The results contained in this and the two following papers were presented before the Pacific Division of the American Association for the Advancement of Science at the Pasadena Meeting, June, 1941.

(2) (a) Curtius, *J. prakt. Chem.*, [2] **91**, 23 (1915); (b) Diels, Blom and Koll, *Ann.*, **443**, 242 (1925); (c) Alder and Stein, *ibid.*, **514**, 211 (1934). However, in the case of the 1,3-cyclohexanedicarboxylic acids, Skita and Rössler [*Ber.*, **72**, 461 (1939)] claim that the same diurethan results both from the cis- and from the trans-diazide.

(3) Fuson and Kao, This Journal, **51**, 1536 (1929); Ellingboe and Fuson, *ibid.*, **56**, 1774 (1934).

(4) Hurd in Gilman's "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1938, p. 698. From succinic acid a small yield of ethylenediamine has been obtained (Oesterlin, *Angew. Chem.*, **45**, 536 (1932)).