

happening without any special catalyst is shown by the fact that the same reaction occurs to a small extent in a Pyrex vessel and, as shown, on alumina and thoria. The reaction goes to a larger extent when dehydrogenating conditions are present. Save for the cracking reactions, the conversion of heptane to toluene is quantitative on chromic oxide gel with sufficient contact time.<sup>3</sup>

The data on the aromatization of the olefins agree with the results from isomerization experiments. The 6-carbon branched chain olefins, while giving only 32% aromatics as compared with 90% for the straight chain compound under the same conditions, are all quite similar. It has been shown that isomerization from one branched olefin to another is rapid at this temperature with the methyl group tending to centralize. The reason for the comparatively low yield must be the necessary isomerization to and low concentration of the straight chain olefin. This is further borne out at the lower temperature where isomerization is slower, and the differences of structure of the starting materials have more influence. The 2-methylpentene-2 isomer gives a better conversion to benzene than does either 2-ethylbutene-1 or 3-methylpentene-2-*t*, two isomers which have

(3) Moldavski and Kamusher, *Bull. Soc. Acad. Sci., U. S. S. R. (N. S.)*, 1936, have shown that *n*-heptane, *n*-octane, and *n*-hexane cyclize on chromic oxide gel but not on thoria, alumina, uranium oxide, zinc oxide, nickel chromate and floridin. Subsequent work by the present writers will show that cyclization actually does occur on special preparations of uranium oxide which have marked dehydrogenation properties.

been shown to be about equal in rate of reaction on an active surface. The reason seems to be that there is one step less to the straight chain from the 2-methyl than from the 3-methyl isomer.

The other properties of the olefins can be summarized similarly. Both liquid and gaseous products show the occurrence of disproportionation at the lower temperatures. As the evolution of hydrogen decreases with decreasing temperature, hydrogenation to saturates begins and poisoning increases. The olefin content of the off-gas at lower temperatures is small and the liquid products have a higher concentration of saturates.

### Summary

1. The dehydrogenation of cyclohexene and 1,3-cyclohexadiene on chromic oxide gel surfaces has been investigated.

2. The influence of character of catalyst on aromatization has been shown. For the conversion of aliphatic hydrocarbons to aromatic hydrocarbons, a dehydrogenating catalyst must be used.

3. The influence of structure of olefin on poisoning, aromatization and disproportionation has been demonstrated.

4. Conclusions concerning isomerization drawn from these experiments agree with those found on other catalysts.

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## The Electron Diffraction Investigation of the Structure of Benzene, Pyridine, Pyrazine, Butadiene-1,3, Cyclopentadiene, Furan, Pyrrole, and Thiophene

BY V. SCHOMAKER AND L. PAULING

The determination of values of interatomic distances in molecules has been found to provide much information regarding electronic structure, especially in the case of substances which resonate among two or more valence-bond structures. The interpretation of interatomic distances in terms of the types of bonds involved is made with use of an empirical function formulated originally for single bond-double bond resonance of the carbon-carbon bond.<sup>1</sup> There are given in this

(1) L. Pauling, L. O. Brockway and J. Y. Beach, *THIS JOURNAL*, **57**, 2705 (1935); L. Pauling and L. O. Brockway, *ibid.*, **59**, 1223 (1937).

paper the results of the determination of the configurations of two molecules involving Kekulé resonance, pyridine and pyrazine, of two molecules with conjugated double bonds, butadiene and cyclopentadiene, and of three five-membered heterocyclic molecules, furan, pyrrole, and thiophene, together with the conclusions regarding their electronic structures reached by application of the bond type-interatomic distance function. In addition, because of the improvement in electron diffraction technique since the study of benzene in these Laboratories four years

ago<sup>2</sup> and because of its similarity to pyridine and pyrazine, this substance was re-investigated.

**Experimental Method.**—The diffraction photographs were prepared with the apparatus and technique described by Brockway.<sup>3</sup> Ten or more photographs were made for each substance, the electron wave length used being about 0.0613 Å. and the camera distance 10.83 cm. The values of  $s_0 = 4\pi(\sin \theta/2)/\lambda$  given in the tables are averages of the values found by visual measurement of ring diameters for ten or more films.

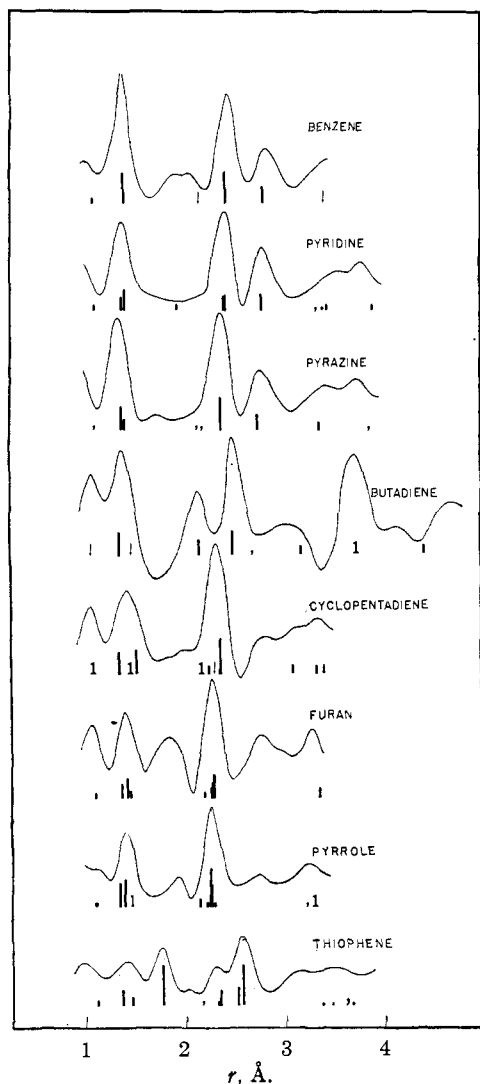


Fig. 1.—Radial distribution curves.

The radial distribution treatment,<sup>4</sup> with refinements soon to be described in THIS JOURNAL, was applied as the first step in the interpretation of the data for each substance. Further selection from among the small range of

(2) L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 867 (1934).

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

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

molecular models compatible with the radial distribution curve for each substance was then made by the usual visual method, involving comparison with simplified theoretical intensity curves for the models under discussion.

The sample of benzene used was prepared by redistilling thiophene-free benzene and rejecting the first and last portions. A similar treatment was given to pyridine (Kahlbaum), pyrrole (Eastman), and thiophene (Eastman). Butadiene was prepared by treating tetrabromobutane in ethyl alcohol solution with granulated zinc and redistilling the product several times. Cyclopentadiene was prepared by distilling dicyclopentadiene; in order that appreciable repolymerization should not take place in the sample the diffraction photographs were made immediately after the distillation (within one hour). Furan was prepared by the decarboxylation of furoic acid and purified by fractional distillation. A sample of pyrazine kindly given us by Professor F. W. Bergstrom was used without further purification.

**Benzene, Pyridine, and Pyrazine.**—New photographs of benzene were obtained showing four more measurable rings than those used in the

TABLE I

BENZENE						
Max.	Min.	<i>I</i>	$C_k^a$	$s_0$	$s^b$	$s/s_0$
1		4	2	3.20	2.89	(0.904) <sup>c</sup>
	2	-10	-7	4.30	4.19	(0.974)
2		10	14	5.71	5.75	1.006*
	3	-1	-2	7.60	7.57	0.996
3		4	11	9.48	9.89	(1.043)
	4	-1	-3	10.26	10.92	(1.063)
4		3	11	11.20	11.15	(0.991)
	5	-7	-27	12.46	12.50	1.003*
5		4	19	13.63	13.89	1.020
	6	-2	-9	14.85	...	...
6		2	10	15.98	15.80	0.989
	7	-5	-23	17.42	17.40	0.999*
7		3	15	18.61	18.84	1.012*
	8	-1/2	-2	20.18	20.29	1.005
8		1 1/2	7	21.30	21.17	0.994
	9	-2	-8	22.70	22.20	0.979
9		2	8	23.80	24.00	1.008
10		1	3	(27.0)	...	...

Average  $s/s_0$  1.002  
 Average deviation 0.008  
 (C-C =  $1.39 \times 1.002 = 1.393$  Å.)  
 (C-H =  $1.075 \times 1.002 = 1.077$  Å.)  
 C-C =  $1.39 \pm 0.02$  Å  
 C-H =  $1.08 \pm 0.04$  Å.

<sup>a</sup> The coefficients of the terms  $(\sin l s_k / l s_k)$  of the radial distribution function. <sup>b</sup> Calculated for coplanar hexagonal model with C-H = 1.075 Å. and C-C = 1.39 Å. <sup>c</sup> Less reliable values, not included in taking the average, are shown in parentheses. <sup>d</sup> The theoretical curve does not indicate a precisely measurable feature at this point. \* In finding the average value of  $s/s_0$ , the starred values are given double weight, for we believe them to be more reliable than the others. Doubly weighted values of  $s/s_0$  are similarly indicated in the following tables.

earlier investigation in these Laboratories. The radial distribution curve calculated with the  $C$  and  $s$  values of Table I (Fig. 1) shows three principal peaks, at 1.37 Å., 2.43 Å. ( $= \sqrt{3} \times 1.40$  Å.), and 2.83 Å. ( $= 2 \times 1.415$  Å.), representing the C-C separations for a regular hexagon with edge about 1.39 Å. The small peaks do not provide reliable information about the C-H bond distance. In order to make an approximate evaluation of this distance, intensity curves were calculated for plane hexagonal models with C-C = 1.39 Å. and C-H varying between 1.00 and 1.18 Å. at intervals of 0.03 Å. These curves (Fig. 2) differ significantly only in the region from the third to the sixth ring. (Note that in the tables a feature of the photographs is for convenience designated by "max." or "min." even though it appears to be a shelf or the inner edge of a shelf, respectively, and that in the text the numbers assigned to the rings correspond to those for maxima in the tables.) The visual intensity estimates for the third and fourth rings have the ratio  $4/3$ ; this is not in accordance with the curves with C-H = 1.12 Å. or more, which make the fourth ring as strong as the third. Moreover, the 1.03 curve (as well as the 1.00 curve) shows only a very poorly defined shelf in place of the fourth ring. The 1.06 and 1.09 curves satisfactorily reproduce all of the features observed on the photographs, including the fifth and sixth rings. The quantitative comparison of observed  $s$  values with those calculated for C-C' = 1.39 Å. and C-H = 1.075 Å. (the mean for the 1.06 and 1.09 curves), given in Table I, leads to C-C =  $1.393 \pm 0.02$  Å. and C-H =  $1.08 \pm 0.04$  Å. This value for the C-H distance agrees well with the value C-H =  $1.090 \pm 0.005$  Å. which may be inferred from the C-H stretching frequencies and our knowledge of the relation of these frequencies to C-H bond distances.<sup>5</sup>

Wierl<sup>6</sup> and Pauling and Brockway<sup>2</sup> have previously reported C-C = 1.39 Å. in benzene. Jones<sup>7</sup> has reported the values C-C =  $1.40 \pm 0.01$  Å. and C-H =  $1.14 \pm 0.01$  Å. It seems probable that the latter value is in error.

An intensity curve was calculated also for a plane trigonal model, with C-H = 1.09 Å., C-C = 1.36 and 1.42 Å. alternately around the ring, the angles C-C-C =  $120^\circ$ , and the angles H-C-C = 123 and  $117^\circ$ , corresponding to quite incomplete resonance between the Kekulé structures. This curve is practically indistinguishable from that for the corresponding plane hexagonal model with C-H = 1.09 Å. and C-C = 1.39 Å. The electron diffraction method is accordingly

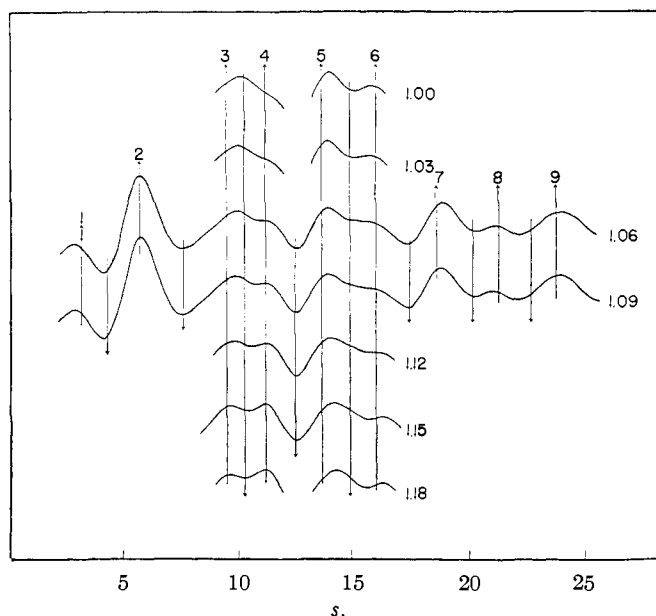


Fig. 2.—Calculated intensity curves for benzene.

unable to add to the existing theoretical and experimental evidence<sup>8</sup> for complete resonance in the benzene molecule.

The photographs obtained for pyridine and pyrazine are so closely similar to those of benzene as to leave no doubt that the three molecules have nearly identical structures. The radial distribution curve for pyridine (Fig. 1) calculated from the data given in Table II has well-defined peaks at 1.38, 2.39 ( $= \sqrt{3} \times 1.38$ ), and 2.76 ( $= 2 \times 1.38$ ) Å. The sharpness of the 2.39 peak indicates that the six meta distances in the ring are nearly equal. The calculated intensity curve for the model with C-C = 1.39 Å., C-N = 1.33 Å., C-H = 1.08 Å., the angle C-N-C =  $119^\circ$  and the angles C-C-C =  $121^\circ$ , and having nearly equal "meta" and "para" distances, is shown in Fig. 3. The comparison of  $s_0$  and  $s$  values for this model (Table II) leads to the values C-H =

(5) E. Eyster, *J. Chem. Phys.*, **6**, 580 (1938).

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

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

(8) C. K. Ingold, *Proc. Roy. Soc. (London)*, **A169**, 149 (1938).

TABLE II  
PYRIDINE

Max.	Min.	<i>I</i>	<i>C</i>	<i>s</i> <sub>0</sub>	<i>s</i>	Model I <sup>a</sup> <i>s/s</i> <sub>0</sub>	Benzene " <sup>1.09</sup> " " <sup>1.39</sup> " <i>s</i> <i>s/s</i> <sub>0</sub>	
1		4	2	3.19	2.99	(0.947)	2.89 (0.906)	
	2	-10	-7	4.37	4.16	(0.952)	4.19 (0.959)	
2		10	14	5.69	5.83	1.025*	5.75 1.011*	
	3	-1	-2	7.58	7.68	1.027	7.57 0.999	
3		4	11	9.14	9.94	(1.087)	9.89 (1.082)	
	4	-1	-3	10.21	10.74	(1.053)	10.92 (1.070)	
4		3	11	11.24	11.30	(1.004)	11.15 (0.992)	
	5	-7	-27	12.73	12.75	1.002*	12.50 0.982*	
5		4	19	13.88	14.23	1.025	13.89 1.001	
	6	-2	-9	15.12	15.85	(1.048)	... ..	
6		2	10	16.20	16.31	1.007	15.80 0.975	
	7	-5	-23	17.60	17.66	1.003*	17.40 .988*	
7		3	15	18.86	19.10	1.013*	18.84 .999*	
	8	-1/2	-2	20.33	20.60	1.013	20.29 .997	
8		1 1/2	7	21.44	21.40	0.997	21.17 .987	
	9	-2	-8	22.65	22.47	0.992	22.20 .980	
9		2	8	23.82	24.27	1.018	24.00 1.007	
10		1	3	28.0	28.18	1.007	... ..	
						Average	1.011	0.994
						Average deviation	0.009	0.010

<sup>a</sup> Models described in text.

1.09, C-C = 1.405, and C-N = 1.344 Å., with average ring bond distance  $1.385 \pm 0.01$  Å. The comparison with the *s* values for a regular hexagonal model leads to the same value 1.385 Å. for the average ring bond distance. It seems unlikely that the C-C distance differs from 1.39 Å.,

tensity curves for model I, with C-C = 1.39 Å., C-N = 1.33 Å., C-H = 1.09 Å., and all ring angles 120°, and for model III, with the same bond distances but with the ring angles at nitrogen 123° and at carbon 118°30', making the meta distances equal, are shown in Fig. 3. These curves, as well as the benzene curve (representing a regular hexagonal model), agree qualitatively with the photographs. The quantitative comparison for all three leads to the value  $1.366 \pm 0.01$  Å. for the average ring bond distance. With C-C = 1.39 Å., this corresponds to C-N =  $1.35 \pm 0.02$  Å.

**Butadiene-1,3 and Cyclopentadiene.**—The photographs of butadiene which were obtained are diffuse and were measured only with difficulty, so that the determination of the configuration of the molecule is less precise than usual. Thirteen rings could be seen, with the *s*<sub>0</sub> and *I* values given in Table IV. These correspond to the radial distribution curve shown in Fig. 1, with peaks at 1.07, 1.38, 2.12, 2.48, (3.0), 3.71, (4.13), and (4.65) Å., the values in parentheses being unreliable. The carbon-carbon peak at 1.38 Å. represents the mean of the values for the two double

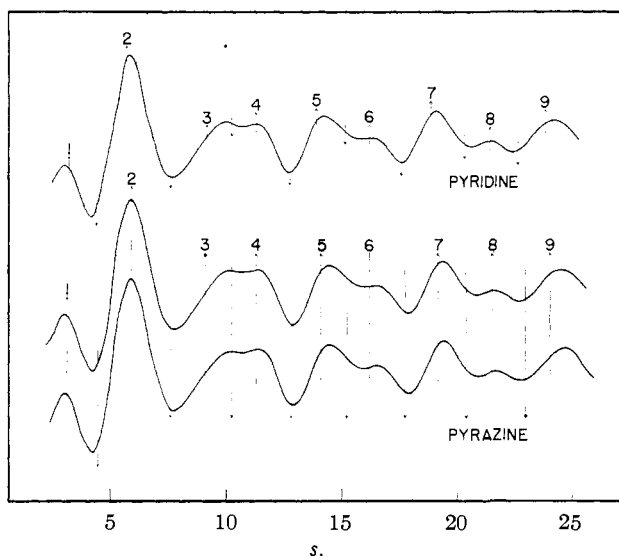


Fig. 3.—Calculated intensity curves for pyridine and pyrazine.

and the results accordingly suggest that the C-N distance is about  $1.37 \pm 0.03$  Å.

The principal peaks on the radial distribution curve for pyrazine (Fig. 1) lie at 1.36, 2.37 ( $= \sqrt{3} \times 1.37$ ), and 2.76 ( $= 2 \times 1.38$  Å.). In-

bonds and the intervening single bond, which has some double bond character. If the double bonds have about the normal distance 1.34 Å. found in ethylene and allene,<sup>1b,5</sup> the value 1.46 Å. is indicated for the conjugated single bond. The peak

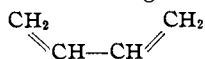
TABLE III  
PYRAZINE

Max.	Min.	<i>I</i>	<i>C<sub>k</sub></i>	<i>s<sub>0</sub></i>	Model I <sup>a</sup>			Model III		Benzene "1.09," "1.39"	
					<i>s</i>	<i>s/s<sub>0</sub></i>	<i>s</i>	<i>s/s<sub>0</sub></i>			
1		4	2	3.09	3.02	(0.977)	3.06	(0.990)	2.90	(0.938)	
	2	-10	-10	4.41	4.23	(.959)	4.20	(0.952)	4.19	(.950)	
2		10	16	5.89	5.87	.996*	5.89	1.000*	5.75	.976*	
	3	-2	-5	7.59	7.77	1.023	7.71	1.016	7.60	1.002	
3		4	12	9.08	10.23	(1.127)	10.24	(1.128)	9.87	(1.087)	
	4	-1/2	-2	10.20	10.70	(1.049)	10.62	(1.042)	10.90	(1.068)	
4		4	16	11.27	11.37	(1.008)	11.35	(1.007)	11.20	(0.994)	
	5	-7	-31	12.76	12.90	1.012*	12.89	1.011*	12.50	.980*	
5		4	19	14.07	14.43	1.026	14.45	1.027	13.93	.991	
	6	-1	-4	15.21	16.02	(1.053)	15.92	(1.047)	...	...	
Shelf	6		2	16.20	16.50	1.018	16.55	1.022	15.80	.975	
	7	-5	-25	17.73	17.90	1.010*	17.95	1.007*	17.40	.982*	
7		3	14	19.16	19.40	1.013*	19.41	1.013*	18.85	.984*	
	8	-1	-4	20.37	20.85	1.024	20.90	1.026	20.30	.997	
8		1	4	21.51	21.60	1.004	21.70	1.008	21.13	.983	
	9	-2	-7	22.97	22.70	0.988	22.78	0.992	22.20	.967	
9		2	6	24.04	24.55	1.021	24.65	1.025	24.00	.988	
						Average	1.012	1.012		0.984	
						Average deviation	0.008	0.008		0.007	

<sup>a</sup> Models described in text. <sup>b</sup> The theoretical curve does not show a measured feature at this point.

at 2.48 Å. corresponds to the 1,3 and 2,4 carbon-carbon distances; this value leads to about 125° for the C=C-C bond angle.

Of the two probable configurations *cis*



and *trans*  $\begin{array}{c} \text{CH}_2 = \text{CH} \\ | \\ \text{CH} = \text{CH}_2 \end{array}$  for the molecule,

the latter is suggested by the presence of a large radial distribution peak at 3.71 Å., which is just the value calculated for the *trans* model. The small radial distribution peak at 3.0 Å. is probably without significance.

The intensity curves I, II, III, and IV of Fig. 4 are calculated for coplanar *trans* models with C-H = 1.06 Å., the angle H-C=C = 115°, and the angle H-C-H = 109.5°. Although these hydrogen parameters are so chosen as to agree as well as possible with minor peaks of the radial distribution function, no great reliance can be placed on them, and indeed it is likely that for this molecule the C-H bond distance is 1.09 Å. The models have the following additional parameters

Model	C=C	C-C	Angle C=C-C
I	1.38 Å.	1.38	126°10'
II	1.36	1.44	124°40'
III	1.34	1.48	123°5'
IV	1.32	1.54	120°10'

The average of the carbon-carbon bond distances has for each model approximately the radial distribution value 1.38 Å. and the angle C=C-C is

such as to give the radial distribution value 2.48 Å. for the 1,3- and 2,4-distances. The agreement with the photographs is reasonably satisfactory for curves II and III, but not for I and IV. For example, the relative intensities of rings 9 and 10 are not well reproduced by curve IV, and those of rings 11 and 12 are not given satisfactorily by either curve I or curve IV. The appearance on the photographs of a doublet (rings 6 and 7) rather than a single ring may be due to an inflection in curves II and III in this region; otherwise the agreement is excellent. Curves were also calculated for about ten models differing slightly from these, with no improvement.

It is concluded that the butadiene molecule has the configuration described by the following parameter values: C-H = 1.06 Å. (assumed), C=C = 1.35 ± 0.02 Å., C-C = 1.46 ± 0.03 Å., angle C=C-C = 124 ± 2°. The configuration is probably essentially coplanar and *trans*; the evidence for this view provided by the radial distribution function is not conclusive inasmuch as it is not supported by a strong dependence of the theoretical intensity curves on the relative rotation of the vinyl groups of the butadiene model. The electron diffraction data are not incompatible with a mixture of *cis* and (predominantly) *trans* molecules. However, other experimental evidence (reviewed by Mulliken<sup>9</sup>) together with theoretical

(9) R. S. Mulliken, *J. Chem. Phys.*, **7**, 121 (1939). See, however, **7**, 373 (1939).

considerations<sup>10</sup> indicates that butadiene molecules must be essentially coplanar and *trans*.

distances, with various ring angles, and with C-H = 1.09 Å. were found to give calculated curves

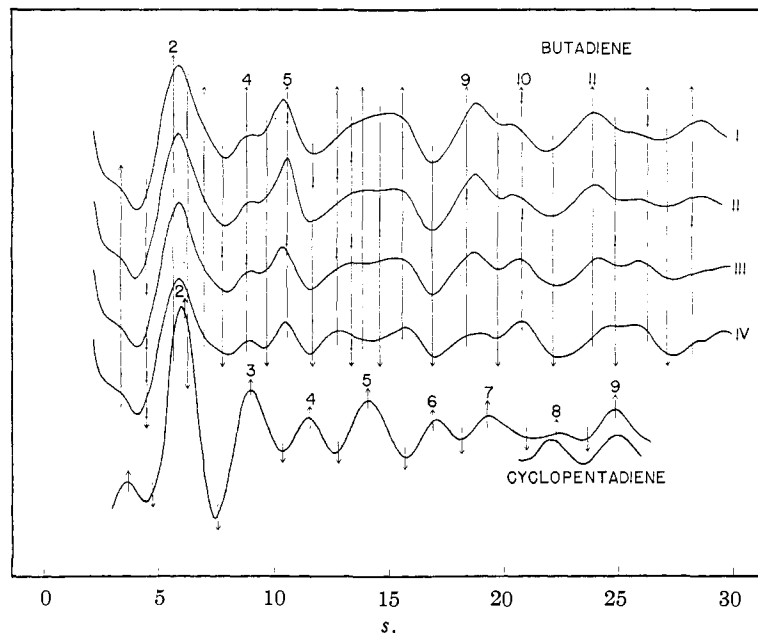
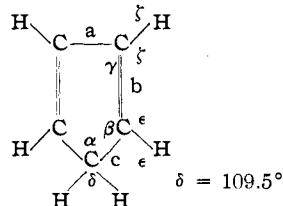


Fig. 4.—Calculated intensity curves for butadiene and cyclopentadiene.

The spectroscopic conclusion of Bartholomé and Karweil<sup>11</sup> that in butadiene there is essentially free rotation about the C-C bond with a barrier not greater than 200 cal./mole is almost certainly incorrect.

Data for the excellent photographs of cyclopentadiene, showing nine rings, are given in Table V. The corresponding radial distribution curve (Fig. 1) has peaks at 1.06, 1.42, and 2.33 Å. The number of parameters determining the structure of this molecule is so great as to prevent their independent evaluation. The molecule



without doubt has the single bond distance  $c$  equal to about 1.53 Å., as in the cycloparaffins, and the double bond distance  $b$  equal to about 1.35 Å., as in butadiene. The conjugated single bond  $a$  is probably about 1.46 Å. Many models with approximately these values for the carbon-carbon

(10) L. Pauling and J. Sherman, *J. Chem. Phys.*, **1**, 679 (1933); W. G. Penney, *Proc. Roy. Soc. (London)*, **A158**, 306 (1937).

(11) E. Bartholomé and J. Karweil, *Z. physik. Chem.*, **B35**, 442 (1937).

showing by their qualitative appearance that  $\alpha = 101 \pm \sim 3^\circ$  and leading on quantitative comparison to the value  $1.445 \pm 0.01$  Å. for the average ring bond distance. This is exactly the average of the values suggested above. Assuming the average of the values of  $b$  and  $c$  to be reliable, we write C-C =  $1.46 \pm 0.04$  Å. as the value determined for the conjugated double bond. The curve shown in Fig. 4, with  $s$  values given in Table V, is that for the model with the values  $a = 1.44$ ,  $b = 1.34$ , and  $c = 1.54$  Å., and the angles  $\alpha = 101^\circ$ ,  $\beta = 109^\circ$ ,  $\gamma = 110^\circ$ . While this curve is slightly better than any of the others we have calculated, it is not possible to base a satisfactory determination of the relative values of the

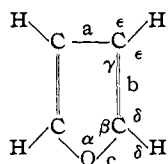
bond distances on the qualitative appearance of the diffraction pattern. The curve gives an excellent representation of the appearance of the photographs except that the fourth minimum of the curve is much too deep relative to the fifth minimum, and the eighth maximum is much too weak. On the films the eighth ring appears to be as strong as the ninth. These discrepancies arise from ignoring the temperature effect,<sup>12</sup> that is, the effect on the diffraction pattern of the variation of the interatomic distances resulting from molecular vibrations. We have found that when probable variations of the various interatomic distances are considered, the slight trouble of the fourth and fifth minima is resolved, as is the greater difficulty of the eighth maximum. This is illustrated for the region of the eighth maximum by the last curve of Fig. 4, which has been plotted for the best cyclopentadiene model (C-C = 1.53, 1.46; C=C = 1.35;  $\alpha = 101^\circ$ ), with the carbon-hydrogen interactions omitted as an approximation to the effect at large diffraction angles of the temperature factor corresponding to the large amplitudes of vibration of the hydrogen atoms.

(12) L. O. Brockway, *Rev. Modern Phys.*, **8**, 238 (1936). The temperature effect may be somewhat significant also for the other molecules discussed in the paper. Its dominating importance for cyclopentadiene is perhaps coincidental. We expect to investigate this question further.



of 1.39 Å. This is substantiated by comparison with calculated intensity curves, which gives  $1.395 \pm 0.01$  Å. for this average.

If the assumption be made that in the molecule



the values of  $a$  and  $b$  are 1.46 and 1.35 Å., respectively, as in butadiene and cyclopentadiene, it is found that there is excellent qualitative and quantitative agreement between the photographs and models with  $C-H = 1.09$  Å.,  $c = 1.41 \pm 0.02$  Å.,  $\alpha = 107 \pm 4^\circ$ ,  $\beta = 109 \pm 3^\circ$ , and  $\gamma = 107 \pm 2^\circ$ , as is illustrated for model XIX by Fig. 5 and Table VI. The quantitative agreement is impaired by change in  $c$ , and the qualitative agreement by change in  $\alpha$  (with corresponding changes in  $\beta$  and  $\gamma$ ). It is interesting to note that

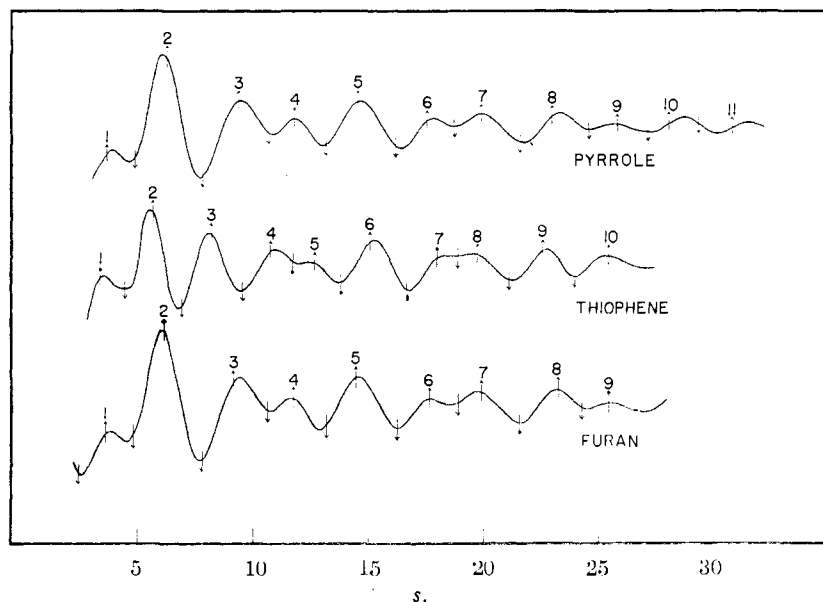


Fig. 5.—Calculated intensity curves for furan, pyrrole, and thiophene.

the value of  $c$  is only slightly less than the single bond  $C-O$  value, 1.43 Å.

The curve for model XIX represents the appearance of the photographs very well, except that the sixth and seventh maxima actually appear to be equally strong. Several of the twenty theoretical curves calculated for furan are nearly as satisfactory, and one, for the model with  $C-O = 1.42$ ,  $C=C = 1.34$ ,  $C-C = 1.44$ , and  $\alpha = 104^\circ$ , is somewhat better, the sixth and seventh maxima on it being equally high. This improvement is probably not significant, especially since the temperature effect may

here play a role as with cyclopentadiene. We find that it is not possible to determine the relative values of the bond distances in the heterocyclic molecules containing only light atoms within reasonable limits by the qualitative comparison, and we have accordingly assumed appropriate values for  $C=C$  and  $C-C$ . For any reasonable given set of ring bond distances qualitative agreement is obtained only when the bond angles are so chosen as to make the cross-ring distances equal to within a few hundredths of an ångström unit.

The photographs for pyrrole are very closely similar to those for furan, and lead to the same value,  $1.395 \pm 0.01$  Å., for the average ring bond distance. The radial distribution function shown in Fig. 1 has important sharp peaks at 1.40 and 2.25 Å. With  $a = 1.46$  and  $b = 1.35$  Å., the average ring bond distance leads to  $c = 1.41$  Å., which is 0.06 Å. less than the  $C-N$  single bond value. In accordance with the discussion given below, it seems probable that this decrease, indicating double bond character, is accompanied by further decrease in  $a$ , and that the values in the molecule are  $C-H = 1.09$  Å.

(assumed),  $a = 1.44$  Å. (assumed),  $b = 1.35$  Å. (assumed), and  $c = 1.42 \pm 0.02$  Å. The angles have the values  $\alpha = 105 \pm 4^\circ$ ,  $\beta = 110 \pm 3^\circ$ , and  $\gamma = 108 \pm 2^\circ$ . The agreement of the photographs with a model falling within this range is shown in Fig. 5 and Table VIII. Other models give the same average ring bond distance.

The data from the photographs of thiophene, showing ten rings (Table VIII), lead to the radial distribution curve of Fig. 1, with peaks at 1.40 Å. ( $C-C$ ), 1.74 Å. ( $S-C$ ), 2.29 Å. ( $C-C$ , meta), and 2.55 Å. ( $S-C$ ). If the

values  $C-C = 1.44$  and  $C=C = 1.35$  Å. be assumed in this molecule, as in pyrrole, the radial distribution curve leads to the configuration with  $S-C = 1.74 \pm 0.03$  Å., angle  $C-S-C = 91 \pm 4^\circ$ , angle  $S-C=C = 112 \pm 3^\circ$ , and angle  $C=C-C = 113 \pm 3^\circ$ . The curve calculated for this model (with  $C-H = 1.09$  Å.) agrees very well with the photographs, as shown in Fig. 5 and Table VIII.

### Discussion

**Pyridine and Pyrazine.**—The values found

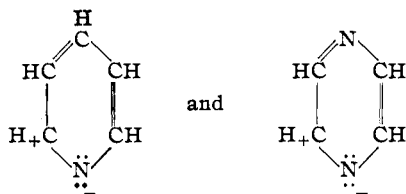


TABLE VII  
PYRROLE

Max.	Min.	<i>I</i>	<i>C<sub>k</sub></i>	<i>s<sub>0</sub></i>	Model <i>I</i> <sup>a</sup> <i>s</i> <i>s/s<sub>0</sub></i>	
1		10	0	3.61	...	(...)
	2			4.85	...	(...)
2		30	8	6.26	6.09	0.972
	3			7.79	7.71	0.989
3		12	7	9.36	9.49	1.014
	4			10.62	10.83	1.019
4		5	7	11.79	11.81	1.001
	5			13.12	13.04	0.994
5		10	22	14.53	14.67	1.009
	6			16.18	16.47	1.018
6		4	13	17.54	17.85	1.017
	7			18.72	18.77	1.003
7		4	15	19.93	19.95	1.001
	8			21.60	21.79	1.009
8		4	17	22.98	23.38	1.017
	9			24.57	24.65	1.003
9		1	4	25.82	25.70	0.995
	10			27.14	27.15	1.000
10		2	7	28.07	28.80	(...)
	11			29.34	30.19	(...)
11		1	3	30.81	31.55	(...)
Average						1.004
Average deviation						0.010
Average ring bond distance						1.395 Å.

<sup>a</sup> Model:  $a = 1.47$  Å.,  $b = 1.34$  Å.,  $c = 1.40$  Å.,  $\alpha = 105^\circ$ ,  $\beta = 110^\circ$ ,  $\gamma = 106^\circ$ .

for the C-N Kekulé-type bond distance in pyridine and pyrazine,  $1.37 \pm 0.03$  Å. and  $1.35 \pm 0.02$  Å., respectively, are somewhat larger than the expected value 1.33 Å. for 50% double bond character. It is possible that this is the result of the large electronegativity of the nitrogen atom, leading to significant additional resonance with ionic structures such as



Probably the effect on the C-N distance is greater for pyridine than for pyrazine because in pyridine there are three structures giving the nitrogen atom a negative formal charge and only single bonds, while in pyrazine there are four such structures of which only two affect a given one of the nitrogen atoms. Investigations of the C-N distances in related compounds such as pyridazine, pyrimidine, and cyanuric and cyameluric<sup>13</sup> derivatives would be of interest in this connection.

(13) L. Pauling and J. H. Sturdivant, *Proc. Natl. Acad. Sci.*, **23**, 615 (1937), have discussed the cyanuric and cyameluric derivatives.

TABLE VIII  
THIOPHENE

Max.	Min.	<i>I</i>	<i>C<sub>k</sub></i>	<i>s<sub>0</sub></i>	Model <i>I</i> <sup>a</sup> <i>s</i> <i>s/s<sub>0</sub></i>	
1		2	0	3.37	3.53	(1.047) <sup>b</sup>
	2			4.42	4.50	(1.019)
2		10	5	5.64	5.52	(0.978)
	3			6.90	6.80	.986
3		8	9	8.17	8.05	.985
	4			9.53	9.50	.997
4		3	5	10.71	10.92	(1.019)
	5			11.70	12.08	(1.032)
5		1	3	12.63	12.42	(0.983)
	6			13.80	13.78	0.999
6		3	11	15.05	15.30	1.016
	7			16.68	16.82	1.008
7		1	5	17.98	18.30	(1.017)
	8			18.88	18.85	(0.998)
8		1	6	19.71	19.60	(0.994)
	9			21.10	21.30	1.009
9		1	9	22.53	22.79	1.010
	10			23.97	24.04	1.003
10		1/2	5	25.41	25.33	0.997
Average						1.001
Average deviation						0.008

<sup>a</sup> Model described in text. <sup>b</sup> Many of the features of the thiophene photographs are of types known to be difficult to measure. Here the inner rings and the components of the two doublets have been thrown out of the average, since measurements of both types of features are known to be unreliable. The effect of the choice of rings to be thrown out is here somewhat greater than usual and may amount to  $\pm 0.005$  in  $s/s_0$ .

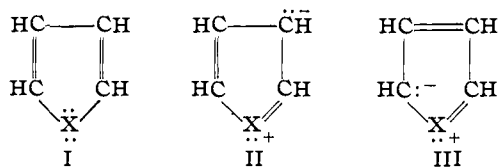
It may be mentioned that this interpretation is in agreement with the deactivating and  $\beta$  directing influence of nitrogen in pyridine and its analogs<sup>14</sup> with respect to substitution reactions.

**Butadiene-1,3 and Cyclopentadiene.**—The value 1.46 Å. for the single bond between conjugated double bonds in butadiene-1,3 and cyclopentadiene has been discussed already in connection with the values found in other hydrocarbons containing conjugated systems.<sup>15</sup> Penney's<sup>10</sup> predicted value for the conjugated bond in butadiene, 1.43 Å., appears to be a little too low.

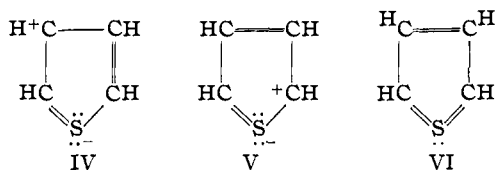
**Furan, Pyrrole, and Thiophene.**—The carbon-heteroatom distances found in furan, pyrrole, and thiophene correspond to  $5 \pm 5\%$ ,  $12 \pm 6\%$ , and  $17 \pm 10\%$  double-bond character, respectively. Resonance of the normal structure I with structures of the types II and III ( $X = O, NH, S$ ) is assumed to be responsible for this double-bond character, while excited structures characteristic

(14) G. W. Wheland and L. Pauling, *This Journal*, **57**, 2086 (1935).

(15) L. Pauling, H. D. Springall, and K. J. Palmer, *ibid.*, **61**, 927 (1939).



of the conjugated system  $\begin{array}{c} \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{C} \end{array}$  together with structures of the type III lead to the shortening of the C—C bond and the lengthening of the C=C bond. The C—C distance is assumed to be 1.46 Å. for furan and 1.44 Å. for pyrrole and thiophene, corresponding approximately to the expected contributions of various structures in these molecules. Besides those already mentioned, we may write for thiophene further reasonably stable structures, of types IV, V, and VI, involving the violation of the octet rule by sulfur, and contributing to the shortening of the C—S and C—C bonds. The



extent of their contribution is discussed below.

It is of interest to compare our results regarding furan, pyrrole, and thiophene with other information about these molecules. First of all, it is understandable that the very electronegative oxygen atom should not like to assume the positive charge of the excited structures written for furan, and that in consequence resonance with these structures should be less important than in pyrrole and thiophene, where the less electronegative atoms nitrogen and sulfur are involved. The values of the stabilizing resonance energy 21, 23, and 31 kcal./mole, respectively, for furan, pyrrole, and thiophene reported by Pauling and Sherman<sup>16</sup> are not in agreement with the great difference of degree of resonance in furan and pyrrole indicated by the electron diffraction investigation. We have recalculated values of the resonance energy from combustion data<sup>17</sup> for several furan and pyrrole derivatives; these values are listed in Table IX, together with our estimates of that part of the resonance energy which is to be attributed to the heterocyclic nuclei, obtained by subtracting the following corrections: 39 kcal./mole for benzene resonance, 6 kcal./mole for con-

(16) L. Pauling and J. Sherman, *J. Chem. Phys.*, **1**, 606 (1933).

(17) M. S. Kharasch, *Bur. Standards J. Research*, **2**, 359 (1929); Landolt-Börnstein, "Tabellen."

TABLE IX  
VALUES OF RESONANCE ENERGY OF DERIVATIVES OF  
FURAN AND PYRROLE

Substance	Resonance energy, kcal./mole	Resonance energy of nucleus, kcal./mole
Furan	23	23
Furfural	29.5	23.5
Furylethylene	28	22
Furfuryl alcohol	32	29
Pyrrrole	23	23
Pyrrrole aldehyde	40	34
N-Phenylpyrrrole	76	31
2,4,5-Trimethyl-3-ethylpyrrrole	33.5	27.5
2,4-Dimethyl-3-ethylpyrrrole aldehyde	42.4	32

jugation with phenyl, vinyl, or aldehyde group, 1.5 kcal./mole for conjugation with methyl or ethyl group, and 3 kcal./mole for conjugation with a hydroxyl group. These values<sup>18</sup> indicate that the resonance energy of the pyrrole nucleus is actually greater than that of the furan nucleus by about 8 kcal./mole, the probable values being approximately 23 and 31 kcal./mole, respectively. It accordingly seems likely that the value given in the literature for the heat of combustion of pyrrole is about 8 kcal./mole high.

The new value for the resonance energy of pyrrole is just equal to that for thiophene. Unfortunately we have been unable to find combustion data for derivatives of thiophene to use in verifying the thiophene value. The interatomic distance data indicate greater resonance for thiophene than for pyrrole, which presumably would be accompanied by greater resonance energy; it is possible, however, that the magnitude of the resonance integrals for a molecule involving a heavier atom (sulfur) is less than for molecules containing only light atoms, and that the resonance energies of thiophene and pyrrole cannot be directly compared to obtain the relative amounts of resonance in the two molecules.

The electric dipole moments in units  $1 \times 10^{-18}$  e. s. u. of these molecules and their derivatives by hydrogenation measured<sup>19</sup> in benzene solution are the following: furan, 0.670; 2,5-dihydrofuran, 1.53; tetrahydrofuran, 1.68; pyrrole, 1.80; pyrroline, 1.42; pyrrolidine, 1.57; thiophene, 0.54; and tetrahydrothiophene, 1.87. We now give a very rough interpretation of these quantities based on the bond moments given

(18) Our recalculation for furan itself led to a small change from the value given by Pauling and Sherman.

(19) H. de Vries Robles, *Rec. trav. chim.*, **58**, 111 (1939); appendix to Symposium, *Trans. Faraday Soc.*, **30**, 904 (1934).

TABLE X  
 SUMMARY OF DISTANCES AND ANGLES

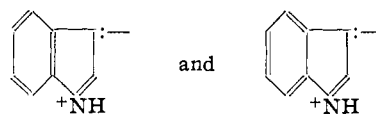
	C-H, Å.	C-C, Å.	C-X	C=C	Angle CXC	Angle XC=C	Angle C=C-C
Benzene	1.08±0.04	1.39±0.02	.....	.....	...	...	...
Pyridine	1.09	1.39	1.37±0.03	.....	} Angles ~ 120°, "meta" distances approximately equal }		
Pyrazine	1.09	1.39	1.35±.02	.....			
Butadiene <sup>a</sup>	1.06	1.46±.03	.....	1.35±0.02			
Cyclopentadiene	1.09	1.46±.04	1.53	1.35	101±4°	109±3°	110±2°
Furan	1.09	1.46	1.41±.02	1.35	107±4°	109±3°	107±2°
Pyrrole	1.09	1.44	1.42±.02	1.35	105±4°	110±3°	108±2°
Thiophene	1.09	1.44	1.74±.03	1.35	91±4°	112±3°	113±3°

<sup>a</sup> Probably coplanar *trans* configuration.

by Smyth<sup>20</sup> and on the usual approximate treatment<sup>21</sup> of the effect on electric dipole moment of resonance with polar structures. A simple calculation suggests that the difference 0.15 *D* in moment between the dihydro and tetrahydro derivatives of furan and pyrrole may be accounted for as the result of change in the direction and number of C-H bonds having moments of about 0.4 *D*. The differences of moments of tetrahydrofuran and furan, and tetrahydrothiophene and thiophene, which are 1.01 and 1.33 *D*, respectively, consist of contributions of 0.05 to 0.10 *D* due to the change of C-H moments, combined with resonance moments, in the same direction, of about 0.95 and 1.25 *D*, respectively, the effects of changing the angles in the ring being neglected. The interpretation of the moments of the pyrroles is complicated by uncertainty regarding the orientation of the N-H bond in these molecules. It seems to be impossible to make a reliable estimate of the resonance moment for pyrrole; various methods of making the calculation give values lying between 1.0 and 2.5 *D*, with 1.5 *D* the most probable value. These resonance moments, 0.95 *D* for furan, 1.5 *D* for pyrrole, and 1.25 *D* for thiophene, correspond to approximately the following total contribution of structures of Types II and III (assumed to be equally important): furan 15%, pyrrole 23%, and thiophene 16%, while the assumed C-X distances correspond to total contributions by excited structures of 10, 24, and 34%, respectively. The agreement of the estimates made in the two ways is reasonably good for furan and pyrrole. The low value found for thiophene by the dipole moment calculation indicates that structures of types IV, V, and VI are of considerable significance; the consideration of the data suggests about 10% contribution by these structures,

involving more than eight electrons in the outer shell of the sulfur atom, and 20% by the structures of types II and III.

Finally, it may be said that the general chemical behavior of furan, pyrrole, and thiophene indicates this order of increasing stability and aromatic character, in agreement with this discussion. An interesting example which seems to support this conclusion is the reaction<sup>22</sup> with maleic anhydride of furan to give (by the Diels-Alder reaction) a product which does not contain the furan nucleus, and that of pyrrole<sup>23</sup> to give in part by a simple condensation a compound in which the pyrrole nucleus is retained. The  $\alpha$  directing influence on substitution reactions of the hetero atoms in furan, pyrrole, and thiophene indicates that excited structures of type III predominate over those of type II, as would be expected from their smaller charge separation. It is interesting to note that  $\beta$ -substitution occurs in indole; this is the result of the fact that of the ionic excited structures, two



place a negative charge on the  $\beta$ -carbon atom, whereas only one such structure occurs for each of the other carbon atoms. This striking difference between pyrrole and indole thus has a simple explanation in terms of resonance.

We wish to thank Professor F. W. Bergstrom for the sample of pyrazine, Dr. W. E. Vaughan for that of tetrabromobutane, Dr. K. J. Palmer for his help with experimental work, Dr. Sidney Weinbaum for assistance in the preparation of the figures, and Dr. E. R. Buchman for discussion of the chemical properties of the substances. We are especially indebted to Professor L. O.

(20) C. P. Smyth, *THIS JOURNAL*, **60**, 183 (1938).

(21) See L. E. Sutton, *Trans. Faraday Soc.*, **30**, 789 (1934).

(22) O. Diels and K. Alder, *Ber.*, **62**, 554 (1929).

(23) O. Diels and K. Alder, *Ann.*, **486**, 211 (1931).

Brockway for checking our measurements of the photographs, for general assistance, and for many helpful discussions.

### Summary

The results of the electron diffraction investigation reported in this paper are collected in Table X. The re-investigation of benzene confirms the value 1.39 Å. for the C-C distance and provides a rough experimental value for the C-H distance. In pyridine and pyrazine the C-N distance is greater than expected for Kekulé resonance; the effect is attributed to extra reso-

nance with ionic structures. The electron diffraction results, electric dipole moment data, resonance energies, chemical information, and simple theoretical considerations indicate, almost uniformly, the order furan < pyrrole < thiophene for the degree of resonance stabilization of these molecules. The contributions of excited structures, other than those characteristic of the conjugated double bonds, are about 10, 24, and 34%, respectively. Part of the resonance of thiophene is with structures with ten electrons in the valence shell of the sulfur atom.

PASADENA, CALIFORNIA

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[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

## Naphthylaminoalkanes

BY F. F. BLICKE AND CHARLES E. MAXWELL<sup>1</sup>

A number of phenyl and hydroxyphenyl substitution products of aminoethane and aminopropane such as epinephrine, neosynephrin, ephedrine and benzedrine have found extensive use as therapeutic agents.

Since there seems to be little information in the literature relative to the pharmacological activity of naphthyl analogs of compounds such as are mentioned above, we have prepared six naphthylaminoalkanes which, with the exception of  $\alpha$ -naphthylaminomethane, have been examined in the form of their hydrochlorides by Mr. L. W. Rowe of Parke, Davis and Company. It was found that the amines exhibited only a slight pressor activity upon initial intravenous injection in dogs with the development of tolerance to succeeding injections. An interesting property shown by the whole group is the production of a "cross tolerance," that is, little or no effect on blood pressure is produced by the administration of ephedrine if the injection of the latter is preceded by an injection of one of the naphthylaminoalkanes.

It seems that more effective compounds might be obtained by the introduction of hydroxyl groups into the naphthalene nucleus; however, Windaus and Bernthsen-Buchner<sup>2</sup> stated that  $\alpha$ -[1-(4-hydroxynaphthyl)]- $\beta$ -aminoethane exhibits only slight pharmacological activity.

(1) This paper represents part of a dissertation to be submitted to the Horace H. Rackham School of Graduate Studies by C. E. Maxwell in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

(2) Windaus and Bernthsen-Buchner, *Ber.*, **50**, 1120 (1917).

$\alpha$ -Naphthylaminomethane,  $\alpha$ -C<sub>10</sub>H<sub>7</sub>CH<sub>2</sub>NH<sub>2</sub> (I), was obtained by interaction of  $\alpha$ -naphthylmethyl chloride and hexamethylenetetramine in chloroform.<sup>3</sup>

In order to obtain 1-( $\alpha$ -naphthyl)-1-aminoethane,  $\alpha$ -C<sub>10</sub>H<sub>7</sub>CH(NH<sub>2</sub>)CH<sub>3</sub> (II), 1-( $\alpha$ -naphthyl)-1-aminopropane,  $\alpha$ -C<sub>10</sub>H<sub>7</sub>CH(NH<sub>2</sub>)CH<sub>2</sub>CH<sub>3</sub> (IV) and 1-( $\alpha$ -naphthyl)-1-aminobutane,  $\alpha$ -C<sub>10</sub>H<sub>7</sub>CH(NH<sub>2</sub>)CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> (VI),  $\alpha$ -naphthylmagnesium bromide was allowed to react with aceto-, propio- and butyronitrile, respectively. The ketones, prepared in this manner, were converted into the oximes and the latter reduced to the amines with sodium and alcohol.

1-( $\beta$ -Naphthyl)-1-aminoethane,  $\beta$ -C<sub>10</sub>H<sub>7</sub>CH(NH<sub>2</sub>)CH<sub>3</sub> (III), was synthesized by reduction of  $\beta$ -acetonaphthone oxime.

The naphthyl analog of benzedrine, 1-( $\alpha$ -naphthyl)-2-aminopropane,  $\alpha$ -C<sub>10</sub>H<sub>7</sub>CH<sub>2</sub>CH(NH<sub>2</sub>)CH<sub>3</sub> (V), was obtained by the following series of reactions: diethyl malonate  $\rightarrow$  diethyl  $\alpha$ -naphthylmethylmalonate  $\rightarrow$  diethyl methyl- $\alpha$ -naphthylmethylmalonate  $\rightarrow$  methyl- $\alpha$ -naphthylmethylmalonic acid  $\rightarrow$   $\beta$ -( $\alpha$ -naphthyl)-isobutyric acid  $\rightarrow$   $\beta$ -( $\alpha$ -naphthyl)-isobutyramide  $\rightarrow$  1-( $\alpha$ -naphthyl)-2-aminopropane.

$\beta$ -( $\alpha$ -Naphthyl)-isobutyric acid (IX) was prepared by a second method according to which  $\alpha$ -naphthaldehyde was condensed with methyl ethyl

(3) For a discussion of this interesting reaction see Heidelberger, "An Advanced Laboratory Manual of Organic Chemistry," The Chemical Catalog Company, New York, N. Y., 1923, p. 24.