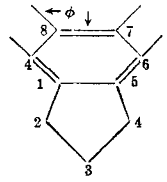
[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY
No. 795]

A Structural Investigation of the Mills-Nixon Effect. The Electron-Diffraction Study of the Structure of 1,3,5-Tribromobenzene, o-Dibromoxylene, o-Dibromohydrindene, and o-Dibromotetralin

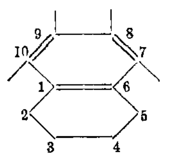
BY ALEXANDER KOSSIAKOFF[1] AND H. D. SPRINGALL

Introduction

The bond angles in a molecule containing a saturated five or six membered ring fused to benzene cannot all be "normal"—109°28′ in the aliphatic portion and 120° in the aromatic. The distortion of the bond angles in these molecules would be expected to produce a differentiation in energy between the resonance structures possessing a single bond and those possessing a double bond in common with the two rings. In hydrindene, the strain produced by the five membered ring would favor resonance structures in which the bond common to both rings is a single bond. In tetralin, the strain produced by the six membered ring is in the opposite direction and would stabilize structures with a double bond in this position. In particular, there would be a differentiation between the two Kekulé structures; the preferred structure for each molecule is shown



hydrindene



tetralin

In order to determine whether or not this effect exists, Mills and Nixon[2] studied the direction of substitution of 7-hydroxyhydrindene and of 8-hydroxytetralin. Their experiments proved that substitution took place exclusively in the manner predicted by the theory. They inferred, therefore, that the double bonds in hydrindene and in tetralin are frozen in the particular Kekulé structure in which the bond angles are the least strained.

The original conclusions of Mills and Nixon should be amended in the light of the modern theory of benzene substitution.[3] According to this viewpoint, the substitution is effected through an excited ionic structure of the benzene molecule which has a free electron pair on the position being attacked. The results of Mills and Nixon should, therefore, be applied to these excited structures instead of to the Kekulé structures making up the normal state of the molecules. This modification, however, in no way affects the principal conclusion that structures which possess the least strain are the most stable. The details of the argument will be discussed in the latter part of the paper.

In view of the great sensitivity of the chemical reactivity of molecules to their electronic structure, the results of Mills and Nixon can be interpreted as showing the direction but not the magnitude of the effect of strain on the benzene ring. Several investigations have been made in order to gain an insight into the actual magnitude of the Mills-Nixon effect. Fieser and Lothrop[4] attacked the problem by blocking the preferred substitution positions in 7-hydroxyhydrindene and in 8-hydroxytetralin by methyl groups. The hydrindene derivative did diazotize in the 6-position, but with considerable difficulty. The tetralin derivative diazotized readily in the 9 position. From these results, Fieser and Lothrop concluded that in neither case was the effect of strain overwhelming, being in fact quite small in tetralin.

In 1935 Sutton and Pauling[5] published an approximate quantum mechanical treatment of the problem. They found that theory predicts a stabilization of one Kekulé structure over the other in hydrindene and in tetralin, but only to the extent of about 10%, the strain energy being small compared to the resonance energy of the molecule. They also calculated the change in the external bond angles on the opposite side of the benzene from the fused ring, the effect being less than 1°.

It can be shown that the angle between a single and a double homopolar bond should be about 125° as compared to the angle between two single

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(1) American Can Co. Fellow. Present address: Department of Chemistry, The Catholic University of America, Washington, D. C.

(2) W. H. Mills and I. G. Nixon, *J. Chem. Soc.*, 2510 (1930).

(3) G. W. Wheland and L. Pauling, THIS JOURNAL, **57**, 2086 (1935).

(4) L. F. Fieser and W. C. Lothrop, *ibid.*, **58**, 2050 (1936).

(5) L. E. Sutton and L. Pauling, *Trans. Faraday Soc.*, **31**, 939 (1935).

bonds of 109°28′. This is given directly by the tetrahedral bond model in which the double bond is represented by two tetrahedra sharing an edge.[6] With this property in mind, Sidgwick and Springall[7] measured the dipole moments of 4,5-dibromo-*o*-xylene, 7,8-dibromohydrindene, and 8,9-dibromotetralin in an effort to obtain a quantitative measure of the Mills–Nixon effect. (These compounds will henceforth be referred to as *o*-dibromoxylene, *o*-dibromohydrindene, and *o*-dibromotetralin, respectively.) The moments due to the two C–Br groups were calculated to be 2.13, 1.78, and 2.11 *D*, respectively, as compared with 2.12 for *o*-dibromobenzene.[8] Assuming that vector addition of bond moments holds for these molecules, the authors concluded that the C–C–Br angles (angles ϕ in the first figure) are normal in the substituted xylene and tetralin, but are more than 5° larger in hydrindene, corresponding to the complete fixation of double bonds in the latter compound.

The experimental and theoretical importance of the problem suggested a direct study of the structures of the bromo-substituted compounds by the electron-diffraction method. 1,3,5-Tribromobenzene, which has already been studied by this method by de Laszlo,[9] was also included in this investigation.

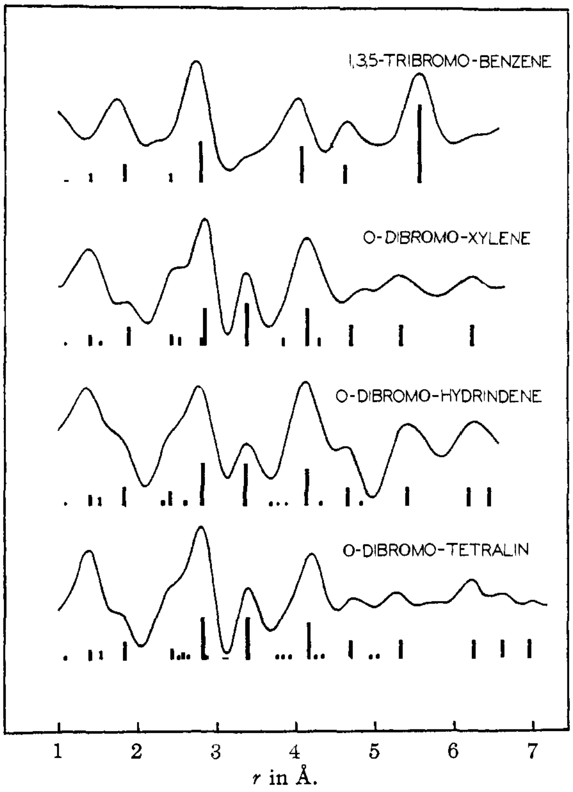

Fig. 1.—Radial distribution curves.

Preparation of Materials.—*o*-Dibromoxylene, *o*-dibromohydrindene, and *o*-dibromotetralin were prepared by the methods given by Sidgwick and Springall.[7]

1,3,5-Tribromobenzene was prepared from 2,4,6-tribromoaniline[10] by the method of Jackson and Bentley.[11] It crystallized from alcohol, being obtained as colorless needles, m. p. 121° (Jackson and Bentley gave m. p. 120–122°).

Experimental Method.—The diffraction photographs were taken using the apparatus and technique described by Brockway.[12] The wave length of the electrons was determined from transmission photographs of gold foil and was approximately equal to 0.06 Å. The camera distances used were approximately 10 cm. and 20 cm. The high boiling points of the compounds necessitated the use of a high temperature nozzle.

Interpretation.—The photographs showed nine or more measurable maxima. The radial distribution treatment[13] was first applied to the data, using the measured positions of the minima as well as of the maxima.

$$R(d) = \sum_n C_n \frac{\sin d s_n}{d s_n}; \quad C_n = f(I_0, s_n); \quad s = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}$$

The coefficients C_n were determined from the visually estimated intensities I_0 in the manner described by Schomaker.[14] The resulting curves for the four compounds investigated are shown in Fig. 1.

The scattering power of a bromine atom is nearly six times that of a carbon atom, and hence the dominant peaks in the radial distribution curves correspond to the Br–Br and C–Br interactions. Of the six different C–Br distances for the benzene ring, two pairs are virtually identical due to the symmetry of the atomic arrangement, so that only four of these peaks appear, two being of double intensity. Unfortunately, the peak corresponding to the C–Br bond distance is incompletely resolved from the multifold C–C peak and the curves do not provide a direct estimate of its value for the compounds studied. The other

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[6] A similar result is obtained by considering the double bond as being composed of a σ and a π bond, if the σ bond is made shorter (given more *s* character) than the two single bonds.

[7] N. V. Sidgwick and H. D. Springall, *J. Chem. Soc.*, 1532 (1936).

[8] L. Tiganik, *Z. physik. Chem.*, **B13**, 425 (1931).

[9] H. de Laszlo, *Proc. Roy. Soc.* (London), **A146**, 690 (1934).

[10] H. Silberstein, *J. prakt. Chem.*, [2], **27**, 101 (1883).

[11] C. L. Jackson and W. B. Bentley, *Am. Chem. J.*, **14**, 335 (1892).

[12] L. O. Brockway, *Rev. Mod. Phys.*, **8**, 231 (1936).

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

[14] V. Schomaker, Am. Chem. Society meeting, Baltimore, Md., April, 1939.

C–Br peaks are strong and undistorted, and provide a basis for the construction of a model of each molecule which is consistent with all the data. Most important, the Br–Br peak, which determines the C–C–Br bond angles, is clearly resolved.

It will be noticed that the Br–Br peak in the radial distribution curves is always lower than the two-fold C–Br peaks which appear on each side. The scattering power of an atom is proportional to $Z - f$, where Z is the nuclear charge and f the atomic scattering factor, which varies with the angle of scattering. It is generally assumed for simplicity that the ratio of $Z - f$'s for two atoms is equal to the ratio of Z's, but this assumption is good only for members of the same row in the periodic table. In the case of bromine and carbon, this ratio is very far from the value 35/6, particularly around $s = 4$, where it is only half this value. These considerations necessitated the use of $Z - f$ ratios in constructing the theoretical intensity curves, these being calculated for each value of s from the tables of Pauling and Sherman.[15] The inapplicability of Z ratios was apparent also from the theoretical curves, where their use produced curves which clearly deviated from the photographs in the region of small s values.

The desire to obtain a direct measure of the C–Br bond distance prompted an attempt to eliminate the interfering distances from the radial distribution treatment. The method by which this was accomplished is applicable to other complicated molecules and is, therefore, described below.

An experimental scattering curve was drawn, using the measured positions of the features and their estimated intensities. The theoretical intensity curves for each compound were used to determine the height of the first strong peak (at $s = 5$), and the general decrease in intensity with increasing s values—these being properties which are insensitive to moderate changes in the assumed atomic arrangement. The resulting curve was taken to represent the "observed" scattering curve for the molecule.

In the elimination of the Br–Br, Br–H, C–C, and C–H interactions it was necessary to establish that the final result is independent of small differences in the assumed distances. Values ranging 0.02 Å. on each side of the Br–Br distance obtained in the original radial distribution calculation were taken, and the C–C distance in the benzene ring was varied from 1.39 to 1.43 Å. The aliphatic C–C distance was kept at 1.54 Å. and the C–H distance at 1.09 Å. A number of intensity curves for these distances were calculated for each molecule, and each was subtracted from the "observed" intensity curve for that molecule. The positions and intensities of the maxima and minima of the resulting curves were used to construct radial distribution curves in the usual manner. All the radial distribution curves for the same molecule looked exactly alike and yielded C–Br distances agreeing with each other to within 0.01 Å. One curve for each molecule is shown in Fig. 2. It will be observed that a strong peak now appears at the C–Br bond distance permitting the estimation of this quantity. The remaining C–Br peaks have positions differing only slightly from those in the original radial distribution curves.

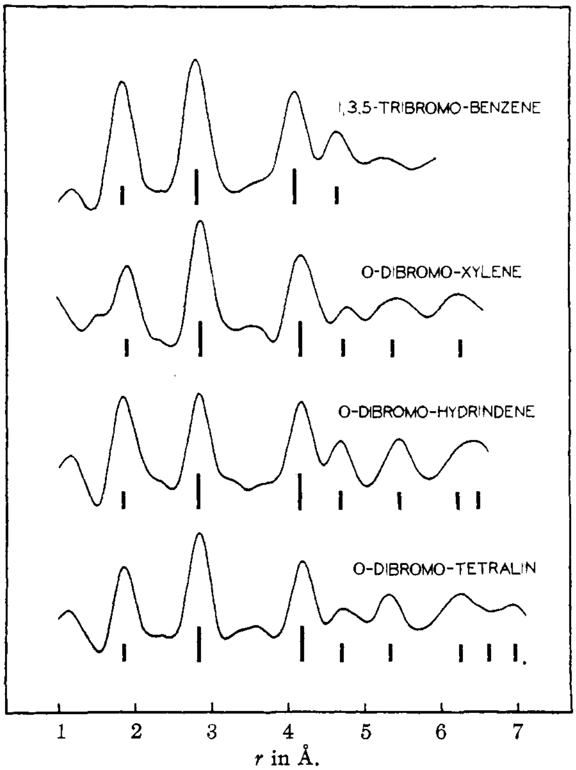

Fig. 2.—Radial distribution curves for C–Br interactions.

Intensity Curves.—The intensity curves were calculated using the formula

$$I(s) = \sum_i \sum_j \frac{(Z - f)_i (Z - f)_j}{(Z - f)_C^2} \frac{\sin sr_{ij}}{sr_{ij}} (e^{-as^2})$$

where $(Z - f)_C$ refers to the scattering coefficient of the carbon atom, and r_{ij} is the distance between atoms i and j. The temperature factor e^{-as^2} was used only for the interactions of hydrogen atoms, the values of a being obtained from the vibrational frequencies of C–H bonds as described by Stevenson, Burnham, and Schomaker.[16]

The very small contribution of hydrogen atoms to the total scattering was evaluated by assuming that they are situated at a distance of 1.09 Å. and at normal angles from the atoms to which they are bonded. The established fact that the benzene ring and the atoms to which it is bonded constitute a planar system, together with the symmetry of the molecules, reduces the number of

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(15) L. Pauling and J. Sherman, *Z. Krist.*, **81**, 1 (1932).

(16) D. P. Stevenson, H. D. Burnham and V. Schomaker, THIS JOURNAL, **61**, 2922 (1939).

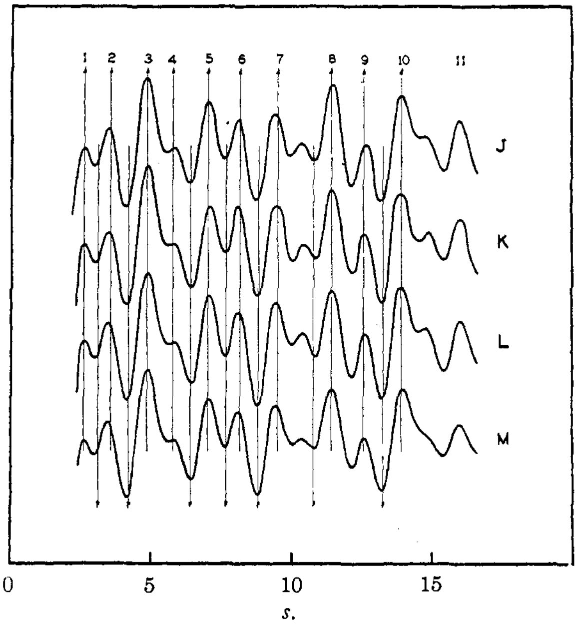


Fig. 3.—Theoretical intensity curve for 1,3,5-tribromobenzene.

parameters which determine the positions of the carbon and bromine atoms in 1,3,5-tribromobenzene, *o*-dibromoxylene, *o*-dibromohydrindene, and *o*-dibromotetralin to 3, 9, 10, and 11, respectively.

The Br–Br distances for the molecules investigated are given to within 0.03 or 0.04 Å. by

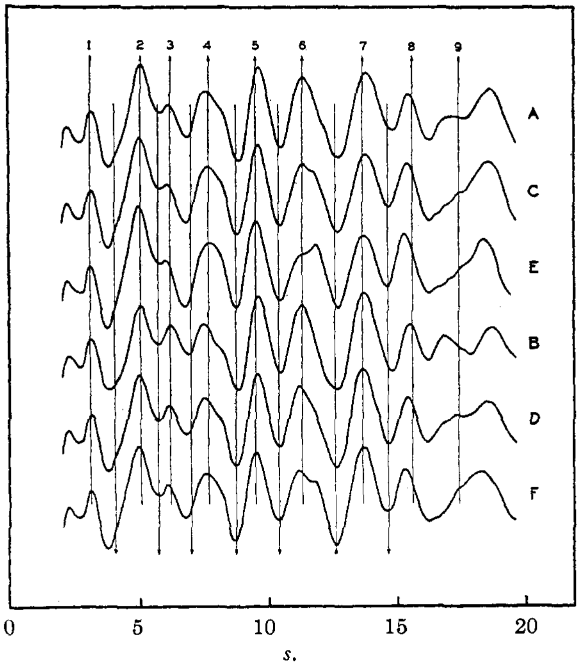


Fig. 4.—Theoretical intensity curve for *o*-dibromoxylene.

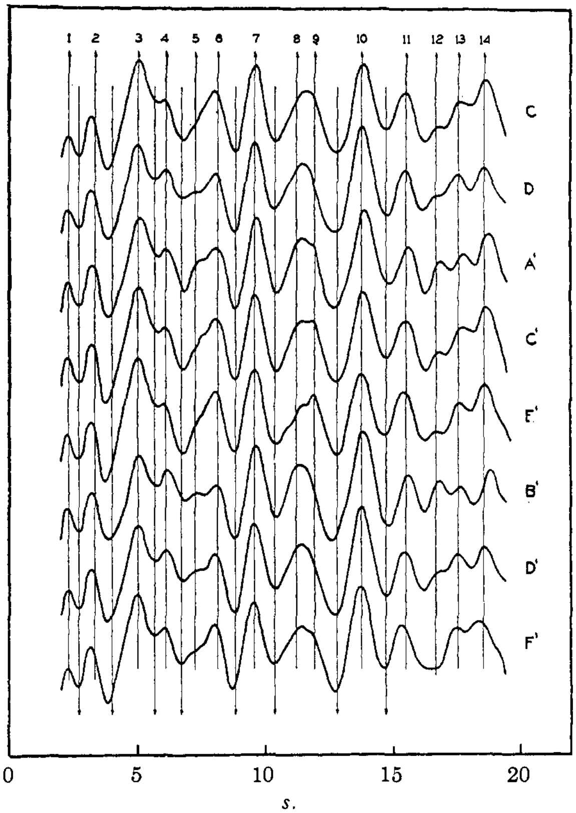


Fig. 5.—Theoretical intensity curve for *o*-dibromohydrindene.

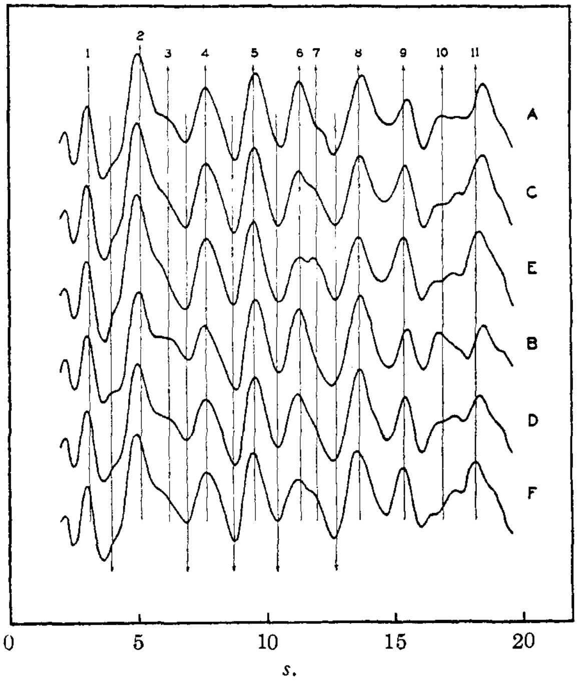


Fig. 6.—Theoretical intensity curve for *o*-dibromotetralin.

the radial distribution curves. It was observed that changing this important distance by as little as 0.02 Å. from the radial distribution value resulted in serious disagreement with the photographs at large *s* values, regardless, within reason, of the assumed arrangement of the carbon atoms. In the case of 1,3,5-tribromobenzene, the symmetry of the molecule makes it possible to explore all the structural possibilities systematically. In the case of the other three molecules, there are too many parameters to determine a unique model. After the construction of a large number of models, it was seen that all those for which the C–Br distances were nearly the same gave identical intensity curves.

TABLE I

1,3,5-TRIBROMOBENZENE

Model	Br–Br	C–C arom.	C–Br	ortho C–Br	meta C–Br	para C–Br	C–CBr–C angle
J	5.59	1.38	1.84	2.81	4.08	4.59	120°
K	5.59	1.41	1.81	2.80	4.10	4.62	120
L	5.59	1.39	1.86	2.79	4.08	4.64	125
M	5.59	1.39	1.84	2.80	4.09	4.62	122
R.D.[a]	5.59	..	(1.76)	2.77	4.08	4.66	
R.D.′[a]	..	..	1.84	2.80	4.08	4.63	

[a] The rows labeled R.D. give the results of the original radial distribution treatment. Those labeled R.D.′ refer to the modified radial distribution treatment described above.

The radial distribution curves are consistent with an entirely symmetrical benzene ring. Since it was found to be impossible to determine whether any dissymmetry exists from the theoretical intensity curves as well, the ring was assumed to be symmetrical in order to permit a determination of the general size of the molecule. This simplification reduces the number of parameters in the dibromo compounds to four. Of the many models tried only the ones with the proper Br–Br distance and a symmetrical ring are shown for these compounds. The permissible deviations of the benzene ring from six-fold symmetry were de-

TABLE II

o-DIBROMOXYLENE, Br–Br = 3.39

Model	C–C arom.	C–Br	ortho C–Br	meta C–Br	para C–Br	H_3C–Br		C–CBr–C angle
A	1.40	1.85	2.82	4.13	4.64	5.34	6.22	123°
B	1.37	1.92	2.85	4.13	4.64	5.32	6.20	122
C	1.44	1.81	2.82	4.16	4.68	5.38	6.26	123
D	1.40	1.88	2.85	4.16	4.68	5.36	6.24	122
E	1.47	1.78	2.82	4.19	4.72	5.42	6.30	123
F	1.44	1.85	2.85	4.19	4.72	5.40	6.28	121
R.D.	..	1.87	2.85	4.16	..	5.32	6.25	
R.D.	..	1.89	2.85	4.16	4.74	5.39	6.21	

TABLE III

o-DIBROMOHYDRINDENE, Br–Br = 3.37

Model	C–C arom.	C–Br	ortho C–Br	meta C–Br	para C–Br		H_2C–Br		C–CBr–C angle
C	1.44	1.81	2.82	4.16	4.68	5.44	6.18	6.50	123°
D	1.40	1.88	2.85	4.16	4.68	5.48	6.20	6.54	122
A′	1.40	1.85	2.82	4.13	4.64	5.39	6.14	6.42	123
B′	1.37	1.92	2.85	4.13	4.64	5.39	6.16	6.44	122
C′	1.44	1.81	2.82	4.16	4.68	5.41	6.18	6.44	123
D′	1.40	1.88	2.85	4.16	4.68	5.44	6.20	6.48	121
E′	1.47	1.78	2.82	4.19	4.72	5.45	6.22	6.48	
F′	1.44	1.84	2.85	4.19	4.72	5.49	6.26	6.52	
R.D.	..	..	2.80	4.15	4.67	5.43			
R.D.′	..	1.84	2.82	4.16	4.68	5.43			

TABLE IV

o-DIBROMOTETRALIN, Br–Br = 3.41

Model	C–C arom.	C–Br	ortho C–Br	meta C–Br	para C–Br		H_2C–Br			C–CBr–C angle
A	1.40	1.85	2.82	4.13	4.64	5.28	6.22	6.54	6.90	123°
B	1.37	1.91	2.85	4.13	4.64	5.30	6.22	6.56	6.92	122
C	1.44	1.81	2.82	4.16	4.68	5.32	6.24	6.58	6.94	123
D	1.40	1.88	2.85	4.16	4.68	5.34	6.26	6.60	6.96	122
E	1.47	1.78	2.82	4.19	4.72	5.36	6.26	6.62	6.96	123
F	1.44	1.85	2.85	4.19	4.72	5.38	6.30	6.66	7.00	121
R.D.	..	..	2.82	4.20	4.73	5.28	6.24			
R.D.′	..	1.85	2.83	4.17	4.70	5.32	6.25			

duced from an analysis of the C–Br distances and will be discussed under "Results." The models used for the final comparison with the photographs were chosen in a systematic manner, as shown in Tables I to IV, in order to permit interpolation. A temperature factor was used in the hydrogen interactions, but not for the distances between the heavier atoms.

The calculated intensity curves are shown in Figs. 3 to 6. The observed intensities and positions of the maxima and minima for the four compounds are shown in Tables V and VI. The average deviations of s/s_0 from the mean for the models finally chosen are: 1,3,5-tribromobenzene 0.003, *o*-dibromoxylene 0.006, *o*-dibromohydrindene 0.005, and *o*-dibromotetralin 0.006. The maximum deviations are 0.007, 0.014, 0.016, and 0.021, respectively, occurring for the structure-insensitive features at low s values.

Discussion of Results

A detailed analysis was made of each intensity curve in respect to its agreement with the position and intensity of each feature in the photographs, and the model for which there was the minimum average deviation was chosen to represent the molecule. The systematic choice of the models allowed an interpolation to be made in the case of *o*-dibromohydrindene and *o*-dibromotetralin, in which the best models were found to lie between C′ and D′ and between D and E, respectively. The resulting values of the interatomic distances are shown in Table VII.

TABLE V

		1,3,5-Tribromobenzene			*o*-Dibromoxylene		
Max.	Min.	I_0[a]	C_n[b]	s_0[c]	I_0[a]	C_n[b]	s_0[c]
1		3	2	(2.60)[c]	7	5	(3.06)
	2	−3	−2	(3.12)	−12	−13	(4.03)
2		9	7	(3.56)	15	20	5.05
	3	−13	−14	(4.21)	−2	−4	(5.72)
3		15	17	4.90	4	7	6.20
	4				−3	−7	6.97
4		2	3	5.76	5	11	7.68
	5	−13	−22	6.39	−6	−18	8.74
5		10	17	7.01	8	20	9.52
	6	−4	−8	7.65	−4	−14	10.39
6		8	14	8.14	5	15	11.32
	7	−8	−16	8.82	−6	−19	12.61
7		9	15	9.49	6	18	13.64
	8	−8	−13	10.75	−3	−12	14.63
8		8	12	11.38	2	7	15.60
9		2	4	12.53	1	4	17.39
	10	−5	−9	13.26			
10		6	8	13.91			

[a] I_0 is the visually estimated intensity. [b] $C_n = f(I_0, s)$, the intensity coefficient used in the radial distribution function (see reference 14). [c] $s = \frac{4\pi}{\lambda} \sin \theta/2$; s_0 represents the observed value of s. Values of s_0 in parentheses were not used in the quantitative comparisons with the calculated values due to the large uncertainties of observation in the region of low s values.

TABLE VI

		o-Dibromohydrindene			*o*-Dibromotetralin		
Max.	Min.	I_0	C_n	s_0	I_0	C_n	s_0
1		7	5	(2.31)	7	6	(3.10)
	2	−7	−6	(2.74)	−15	−15	(3.98)
2		8	8	(3.25)	15	20	5.10
	3	−14	−16	(4.02)			
3		15	20	5.00	2	4	(6.15)
	4	−4	−7	(5.64)	−5	−10	6.87
4		5	9	6.10	6	12	7.66
	5	−7	−12	6.71	−10	−21	8.68
5		3	7	7.24	10	21	9.48
	6				−6	−16	10.40
6		7	14	8.14	6	13	11.29
	7	−8	−19	8.84			
7		10	21	9.55	2	4	11.95
	8	−8	−17	10.38	−9	−17	12.71
8		7	15	11.21	9	19	13.61
9		2	4	11.92	5	9	15.37
	10	−7	−13	12.80			
10		9	18	13.73	1	2	16.87
	11	−5	−10	14.70			
11		4	7	15.48	3	5	18.13
12		1	2	16.65			
13		1	2	17.53			
14		1		18.54			

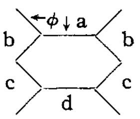
TABLE VII

	1,3,5-Tribromobenzene	*o*-Dibromoxylene	*o*-Dibromohydrindene	*o*-Dibromotetralin
Model	M	D	C′-D′	D-E
Br–Br[a]	5.59 Å.	3.39 Å.	3.37 Å.	3.41 Å.
C–Br[a]	1.84	1.88	1.84	1.86
Av. C–C[a] (arom.)	1.39	1.40	1.42	1.42
C–C–Br angle[a]	119°	122°	122°	122°

[a] All distances are subject to an experimental error of 0.02 to 0.03 Å. The angles are good to about ±2°.

The normal disposition of the carbon atoms in the saturated portion of the molecules (the 3 and 4 carbons in the six-membered ring in the tetralin derivatives were assumed to be out of the plane of the molecule in order to preserve the normal bond angles) seems to agree well with the photographs except in the case of the hydrindene derivative. It was found that the agreement could be markedly improved, particularly for the 9th maximum, by changing the angles adjacent to the benzene ring in the five membered ring from 110° to 112¹/₂°. This change would produce a strain in the bond angles of the saturated ring, but would partially relieve the strain in the benzene ring.

A mathematical analysis of the C–Br distances obtained from the theoretical curves and from the radial distribution treatment indicates that the benzene ring can be distorted in certain ways without destroying the agreement with experiment. If we designate the different C–C distances in the ring by the letters a, b, c, and d, as shown in the figure

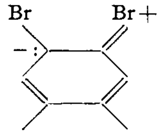


then the results for *o*-dibromoxylene show that alternate pairs, either a and c or b and d, can be made longer than 1.40 Å., the others shorter. In the case of the hydrindene and tetralin derivatives a and d can be made shorter, and b and c longer than 1.42 Å. Unfortunately, these conclusions are negative in character and simply imply that a distortion may exist. On theoretical grounds, it is doubtful if such a distortion could be larger than 0.02 or 0.03 Å.

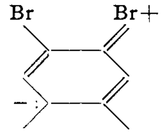
The most striking conclusion obtained from a comparison of the results for the three *o*-dibromo compounds is that they are very similar in structure. They can be described within experimental error by the parameters: C–C = 1.41 ± 0.02 Å.; C–Br = 1.86 ± 0.02 Å; C–C–Br angle = 122 ± 2°. The complete fixation of the double bonds in the hydrindene or the tetralin compound is certainly out of the question, since this would indicate Br–Br distances differing from those observed by 0.30 Å. or more. As a matter of fact, the small differences observed in the Br–Br distances for these compounds are in the opposite direction.

Theoretical Interpretation.—This structural investigation confirms the conclusion of Sutton and Pauling[5] that the fusion of a saturated ring to benzene produces virtually no change in the external bond angles of the benzene ring. The results, however, indicate a large amount of double-bond character for the C–Br bond in the bromo benzenes, particularly in the hydrindene derivative,[17] providing information concerning the relative importance of the excited ionic states in these compounds. It has previously been noted that the chemical results dealing with the Mills–Nixon effect are to be attributed to the differentiation in the energies of the excited ionic structures. In the following discussion it will be shown how the structure and dipole moment results also can be accounted for in a straightforward manner by a consideration of the effect of strain on the ionic states of the molecules in question.

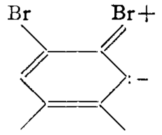
In the dibromo compounds under consideration there are six singly excited ionic structures, three for each bromine atom. The structures differ in the position of the free electron pair and of the double bonds in the ring. Indicating the three structures for a particular bromine atom by the numbers I, II, and III, we have



I



II



III

The vertical components of the dipole moments of these structures are 7.5, 19.0, and 13.3 *D*, respectively, the moment of III being equal to the average of those for I and II. The structures all shorten the C–Br distance toward the double bond value of 1.70 Å.

The effect of these structures is, therefore, to decrease the moment of the molecules and to shorten the C–Br distance. The experimental verification for their importance in determining the properties of the bromobenzenes is the large difference in moment (0.4 *D*) and in the C–Br distance (0.03 to 0.04 Å.) between aromatic and aliphatic bromides.

It is important to notice that structures I and II both have a single bond on the side of the ring opposite the bromine atoms, while structure III has a double bond in this position. In the absence of a fused ring, structures I and III should have the same energy, except for a second order effect involving the difference in electron affinity of the carbon atoms which participate in the resonance. Structure II should have a somewhat higher energy due to the greater charge separation. A fused five-membered ring produces a strain in the molecule which results in decreasing the energy of (stabilizing) structures I and II, and increasing the energy of (destabilizing) III. A fused six membered ring, on the other hand, lowers the energy of III and raises that of I and II, though

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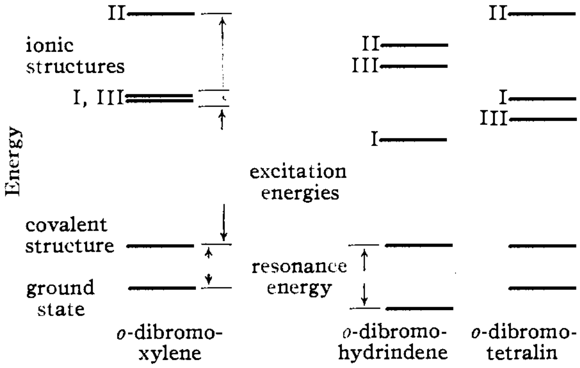
(17) The bond distance was found to be 0.04 Å. shorter than in *o*-dibromoxylene, and 0.02 Å. shorter than in *o*-dibromotetralin. This estimated difference between the C–Br distances in the three compounds might well be more reliable than the absolute values themselves.

the effect is doubtless much smaller as judged from the chemical evidence and from geometrical considerations. On the basis of this splitting of the energy levels, the total contribution of the ionic states should be greatest in *o*-dibromohydrindene and least in *o*-dibromotetralin.

In calculating the total contribution of two excited structures to the normal state of the molecule, it is found that its magnitude is increased by separating the energy of the structures about the mean value. (This result is responsible for the extra ionic energy of heteropolar bonds.) The splitting of the energies of the ionic structures by the fusion of a saturated ring would, therefore, tend to increase the total contribution of these structures. This effect would combine with the favorable splitting in hydrindene to give a large increase in the total contribution of the ionic states, but would partially counteract the already small unfavorable splitting in tetralin, producing an insignificant net effect. These conclusions coincide exactly with the experimental results concerning the dipole moments and bond distances in these molecules.

The above argument can be made clearer by constructing a qualitative energy diagram, giving the energies of the excited ionic states relative to that of the covalent structure, and of their contributions to the energy of the normal states.



It may be noted that in the chemical experiments of Mills and Nixon the position of substitution depends on the relative excitation energies of structures I and III (the Br atoms being replaced by other groups capable of furnishing electrons to the ring, such as OH and NH_2). Their results are directly predicted on the basis of this picture.

Qualitatively, at least, these considerations provide a satisfactory explanation for the results of the structure, dipole moment, and chemical investigations of compounds possessing a saturated ring fused to a benzene nucleus. A semiquantitative quantum-mechanical treatment similar to that of Sutton and Pauling[5] is feasible, but would not be much more convincing than qualitative arguments because of the necessity of making guesses concerning the energies of the ionic states.

Acknowledgment.—The authors are especially indebted to Professor Linus Pauling, who proposed the subject of this investigation. They also wish to express their thanks to Dr. Verner Schomaker and to Dr. David P. Stevenson for their many helpful suggestions and criticisms.

Summary

1. The structures of 1,3,5-tribromobenzene, *o*-dibromoxylene, *o*-dibromohydrindene, and *o*-dibromotetralin have been determined by the electron-diffraction method.

2. The C–Br distance in 1,3,5-tribromobenzene has been found to be 1.84 ± 0.02 Å., 0.04 Å. shorter than that reported by de Laszlo.

3. The C–Br distances in the dibromo compounds have been found to be 1.86 ± 0.02 Å., the C–C–Br angles 122 ± 2°. The individual variations, which are within experimental error, are shown in the table under "Results."

4. A method has been worked out for the elimination of the less important interactions in a complex molecule in order to obtain better values for the important distances from the radial distribution treatment.

5. The results of the structure investigation have been correlated satisfactorily with those of the dipole moment measurements through the consideration of the excited ionic structures of the dibromo compounds.

6. The effect of strain on the benzene molecule (Mills–Nixon effect) has been shown to be concerned primarily with changes in the contributions of excited states of the molecule, and not with freezing the double bonds in the ring into a particular Kekulé structure.

PASADENA, CALIFORNIA RECEIVED FEBRUARY 28, 1941