Summary

1. The adsorption of carbon monoxide and of argon on mica has been determined at −183°. The data for carbon monoxide are in excellent agreement with those of Bawn but are not in accord with those reported by Langmuir, whereas the results with argon show better agreement with Langmuir's data than with Bawn's. At saturation the mica surface is completely covered with a monomolecular layer of carbon monoxide but is only 17% covered with argon.

2. The rate of adsorption is certainly not instantaneous with either gas, indicating that the process is not physical adsorption alone.

3. Two types of adsorption of carbon monoxide were observed. The first, which covers approximately a quarter of the surface, cannot be removed by pumping at −183° but can be taken off only at a higher temperature. The second, which covers the rest of the surface, can be removed by pumping at −183°. It is concluded that argon and the strongly-held molecules of carbon monoxide are adsorbed on active centers and it is suggested that these centers are the points on the mica surface from which a potassium atom is removed on cleavage. Support for this view is obtained from X-ray data.

4. The adsorption of carbon monoxide follows the simple Langmuir isotherm even though the surface is not homogeneous. The adsorption of argon follows the Langmuir equation for two kinds of elementary spaces. Palmer's isotherm represents the results with carbon monoxide but does not fit those for argon.

5. The spreading force of adsorbed carbon monoxide is calculated. It varies with the surface area per molecule in the same way as the spreading force of insoluble films on water. The adsorbed gas follows a two-dimensional van der Waals equation and shows the general behavior characteristic of a two-dimensional gas. The spreading force of adsorbed argon is very small over the entire pressure range investigated.

KEARNY, N. J. RECEIVED NOVEMBER 16, 1937

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Electron Diffraction Investigation of the Molecular Structures of Isobutane, *t*-Butyl Chloride and *t*-Butyl Bromide[1]

BY J. Y. BEACH[2] AND D. P. STEVENSON

The concept of the tetrahedral carbon atom has been an indispensable part of chemistry for many years. For much of that time, however, it remained a hypothesis necessary to account for the number and properties of the isomers of carbon compounds that could be prepared. It was not until the advent of X-ray and electron diffraction methods that the concept was put on a direct quantitative basis. The X-ray investigations of diamond and carborundum afforded the first direct evidence for the tetrahedral carbon atom. More recently electron diffraction methods have been used to prove the tetrahedral form for the gas molecules of carbon tetrafluoride, carbon tetrachloride, carbon tetrabromide, tetramethylmethane and other group IV compounds. Many other molecules, methylene chloride, chloroform, etc., have been shown to be only slightly distorted from tetrahedral symmetry. It is with this question of distortion of tetrahedral angles that we are concerned in the present investigation.

Because of the electrostatic and steric repulsions of the methyl groups it is to be expected that the C–C–C angle in isobutane is greater than the tetrahedral angle (109° 28′). In discussing *t*-butyl chloride and *t*-butyl bromide it is not immediately clear what effect the substitution of a halogen atom for a hydrogen atom will have on the C–C–C angle. The charge on the hydrogen atom, because of the direction of the C–H moment, is positive.[3] The electrostatic attraction of the negative halogen atom for the positive hydrogen atoms would tend to spread the C–C–C angle more than in isobutane. But, on the other hand, the increased steric repulsion between halogen and hydrogen atoms would tend to decrease the C–C–C angle below that in isobutane and possibly below the tetrahedral angle.

Assuming that the charges giving rise to the di-

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[1] These results were presented to the American Chemical Society at Rochester, N. Y., September, 1937.

[2] National Research Fellow in Chemistry.

[3] C. P. Smyth, *J. Phys. Chem.*, **41**, 209 (1937).

pole moments are located at the centers of the atoms it is an elementary calculation to find the electrostatic attraction of the halogen atom for the methyl hydrogen atoms. For the purpose of the calculation a model for the molecule is set up in which all angles are tetrahedral and interatomic distances are those given in the table of covalent radii.[4,5] The maximum attraction of the halogen atom for a hydrogen atom, when the hydrogen atom is as close as possible to the halogen atom, is 1.38 kcal. for the chloride and 1.17 kcal. for the bromide. These values change only by about 12% when the distance between the atoms is increased by rotating the methyl group through 60°.

We have calculated the steric repulsion of chlorine for hydrogen and bromine for hydrogen by the method of Eyring.[6] Using the same molecular model the steric repulsion at the distance of closest approach is 7.2 and 8.0 kcal. for the chloride and bromide, respectively. These repulsions are 2.4 and 3.6 kcal., respectively, when the interatomic distance is increased by rotating the methyl groups through 60°. It is evident from these figures that the steric repulsion is greater than the electrostatic attraction and therefore the C–C–C angle will be decreased in going from isobutane to *t*-butyl chloride or *t*-butyl bromide. We have not calculated and summed the steric repulsions and electrostatic interactions for all the atoms attached to the central carbon atom so we cannot predict which way the angle will be distorted from the tetrahedral value in the two halides. The van der Waals interactions have not been included in the discussion because at these interatomic distances they are negligible in comparison with the interactions considered.

The electron diffraction results are in harmony with the calculations. In none of the compounds is the C–C–C angle distorted from the tetrahedral value by more than about 4°. Our results for the C–C–C angles in these compounds are: for isobutane 113°30′ ± 2°, for *t*-butyl chloride 111°30′ ± 2° and for *t*-butyl bromide 111°30′ ± 2°. This confirms our expectation that the C–C–C angle in the halides is less than in isobutane. The accuracy of the experiment is such that one may say with reasonable certainty that the effect exists. The fact that the C–C–C angle in the two halides is greater than the tetrahedral angle shows that the sum of the electrostatic repulsion between methyl groups, the electrostatic attraction of the halogen atom for a methyl group and the steric repulsion between methyl groups is greater than the steric repulsion of the halogen atom for a methyl group.

Pauling and Brockway[5] have reported an angle of 111°30′ for isobutane, two degrees smaller than our value. However, for reasons which we shall point out later, we regard the 111°30′ angle as unlikely. *t*-Butyl bromide has been investigated by electron diffraction by Dornte,[7] who reported results somewhat different than those presented here. *t*-Butyl chloride has not been investigated previously by electron diffraction.

The carbon–carbon distance and the carbon–halogen distances in these compounds would be expected to be the sum of the single covalent radii.[4] There are no Lewis electronic structures the molecule may possess other than the obvious one. Resonance, therefore, is not to be expected. The carbon–carbon distance in isobutane is found to be 1.54 ± 0.02 Å., the expected value. The carbon–chlorine distance in the chloride and the carbon–bromine distance in the bromide are found to be 1.78 ± 0.03 Å. and 1.92 ± 0.03 Å., respectively. The carbon–chlorine distance is 0.02 Å. longer and the carbon–bromine distance is 0.01 Å. longer than expected from the covalent radius table. These differences in view of the complexity of the molecules probably are not significant. However, from the chemical reactivity of these molecules abnormal distances for these bonds might be suspected. The *t*-butyl halides are hydrolyzed[8] rapidly by water whereas the normal compounds require a strong base for their hydrolysis. The tertiary halides also lose HX readily upon the application of heat[9] in contradistinction to the normal halides. We cannot say that we have observed a lengthening of these bonds over the covalent radius sums.

Method.—The apparatus used in this investigation is closely similar to the one described by Brockway[10] and used by Pauling, Brockway, *et al.*, for determining the structure of gas molecules. The electrons were accelerated by a potential of

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[4] L. Pauling and M. L. Huggins, *Z. Krist.*, **87A**, 205 (1934).

[5] For a revision of some of the double and triple bond radii see Pauling and L. O. Brockway, THIS JOURNAL, **59**, 1223 (1937).

[6] H. Eyring, *ibid.*, **54**, 3191 (1932).

[7] R. W. Dornte, *J. Chem. Phys.*, **1**, 630 (1933).

[8] E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 255 (1935).

[9] G. B. Kistiakowsky and C. H. Stauffer, THIS JOURNAL, **59**, 165 (1937).

[10] For a review of the experimental procedure and a summary of electron diffraction results see Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

roughly 57 kilovolts. The wave length of the electrons was 0.0515 Å. This was found accurately by taking transmission pictures of gold foil, the structure of which is known. In interpreting the photographs we have used the visual method[11] and the radial distribution method.[12]

The formula used in the visual method for calculating the intensity of the scattered electrons as a function of the scattering angle is

$$I = \Sigma_i \Sigma_j Z_i Z_j \frac{\sin sr_{ij}}{sr_{ij}} \qquad (1)$$

where Z_i and Z_j are the atomic numbers of the *i*th and *j*th atoms, r_{ij} is the distance between the *i*th and *j*th atoms, and s is $(4\pi \sin \Theta/2)/\lambda$. Both summations are taken over every atom in the molecule. λ is the wave length of the electrons and Θ is the angle through which the electrons are scattered. To evaluate eq. (1) a model for the molecule is assumed, the r_{ij}'s are calculated from the geometry of the model and put into the formula. The intensity, in arbitrary units, is calculated and plotted in terms of s. This procedure is repeated for a number of molecular models, the number depending on the complexity of the molecule and on the preëxistent ideas regarding its structure. The shape of the intensity curve, that is, the relative heights and spacings of the maxima and minima, is dependent only on the shape assumed for the molecule and not on the assumed size. The size assumed affects only a scale factor which is automatically corrected when the ring diameters of the maxima and minima on the films are compared quantitatively with the positions of the maxima and minima on the theoretical curve. In general many of the models for the molecule can be eliminated from a qualitative comparison of the photographs with the calculated curves. By qualitative comparison is meant a comparison of the relative heights and spacings of maxima and minima between photographs and curves without resorting to measurement of the photographs. The final results are obtained from a quantitative comparison of the photographs with the qualitatively acceptable calculated curves.

The radial distribution method consists of inverting the intensity formula. Instead of calculating the intensity of scattering as a function of the structure, the density of atoms in the molecule is calculated in terms of the observed scattering. This distribution function is obtained directly from measurements on the photographs, no assumption of molecular model being involved. These functions for isobutane, *t*-butyl chloride and *t*-butyl bromide are shown in Fig. 1.

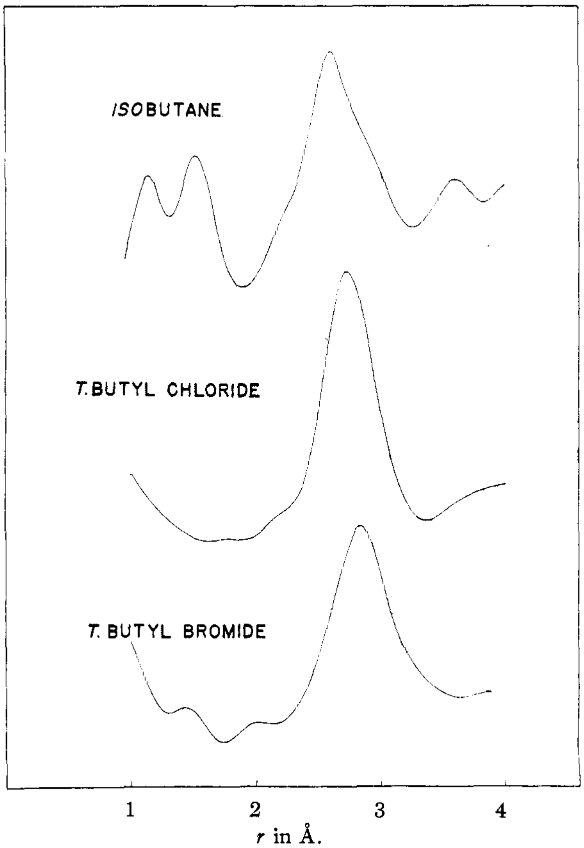

Fig. 1.—Radial distribution curves for isobutane, *t*-butyl chloride and *t*-butyl bromide.

Isobutane.—The isobutane used in this investigation was tank isobutane from the Ohio Chemical Company. It was fractionally distilled several times in a vacuum system before being distilled into the container connected to the apparatus. The photographs, taken with the sample at −36°, show seven maxima. The first two are strong, the second being somewhat stronger. The third and fourth are close together, separated by a deep wide minimum from the fifth which is again separated considerably from the sixth. The seventh maximum is closer to the sixth than the sixth is to the fifth, but is very weak and no very reliable measurements could be made on it. Between the fifth and sixth maxima there is a faint maximum on which no measurements could be made. The visually estimated intensities and the measured values of s are given in the third and fourth columns of Table I.

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[11] Pauling and Brockway, *J. Chem. Phys.*, **2**, 867 (1934).

[12] Pauling and Brockway, THIS JOURNAL, **57**, 2684 (1935).

Table I

Isobutane

Maximum	Minimum	I	$s_{\text{obsd.}}$	$s_{\text{calcd.}}$	C–C, Å.
1		15	2.872	2.78	1.491
	2		4.358	3.90	1.378
2		30	5.364	5.62	1.613
	3		6.991	6.89	1.518
3		8	7.801	8.02	1.583
	4		8.627	8.96	1.599
4		5	9.453	9.63	1.569
	5		11.52	11.23	1.501
5		18	12.82	12.84	1.542
6		10	17.61	17.67	1.545
				Average (1 max. omitted)	1.539

Final results: C–C 1.54 ± 0.02 Å.
C–C–C angle 113°30′ ± 2°.
C–H 1.09 Å. (assumed)

The six term radial distribution function is shown in Fig. 1. It shows maxima at 1.13, 1.53 and 2.60 Å. The first peak represents the carbon–hydrogen single bond distance, the second peak represents the carbon–carbon single bond distance and the third peak represents the long carbon–carbon distance.

Assuming the carbon–hydrogen distance to be 1.09 Å., isobutane has one shape parameter—the C–C–C angle. The calculation of the theoretical intensity curves is complicated by the existence of a large number of interatomic distances in the molecule. The most important distances are the carbon–carbon distances. The next in importance are the carbon–hydrogen distances. The hydrogen–hydrogen distances can be neglected safely. There are two carbon–hydrogen distances that remain constant when the methyl groups rotate; there are three when the C–C–C angle is not assumed to be tetrahedral. These are easily included in calculating the theoretical curves. For a general orientation of a methyl group there are six long carbon–hydrogen distances that vary with the orientation of the methyl group. To include these terms in the calculations requires an assumption regarding the motion of the methyl groups. In calculating intensity curves for neopentane Pauling and Brockway[5] found that the curve calculated for a model having symmetry T is nearly the same as the curve calculated for free rotation of the methyl groups. Their model having symmetry T is obtained from either of the two models having symmetry T_d by rotating the methyl groups through 30° so that the hydrogens fit together like cogs. They found also that the curve obtained for free rotation of the methyl groups is practically indistinguishable from the curve obtained by neglecting the long carbon–hydrogen terms altogether. On the strength of this Pauling and Brockway omitted the long carbon–hydrogen distances in calculating the theoretical curves for isobutane. We have made calculations for isobutane analogous to the ones made for neopentane by Pauling and Brockway. Our results justify their neglect of the long carbon–hydrogen terms. The curves for the free rotation model and a model having the symmetry C_3 are practically identical with the curves obtained by omitting the long carbon–hydrogen distances. The model having symmetry C_3, suggested to us by Professor Pauling, is obtained from either of the two models having symmetry C_{3v} by rotating the methyl groups through 30°. The curves for the models having symmetry C_{3v} in which there are three C–H bonds parallel (or nearly so when the C–C–C angle is not tetrahedral) to the three-fold axis—two hydrogens on each methyl group being *trans* to adjacent methyl groups—are, surprisingly, noticeably different from the other curves. We have made our interpretation of isobutane with curves calculated from models having symmetry C_3. The difference between the angle reported by Pauling and Brockway (111°30′) and the angle reported here (113°30′) is not because of this as the two sets of curves do not differ sufficiently. It is due to a different interpretation of the fourth maximum on the photographs. Pauling and Brockway identify it as a shelf while we prefer to call it a small maximum. The close similarity of the curves for the models having symmetry C_3 and, approximately, a minimum potential energy of the methyl groups to the curves for free rotation of the methyl groups precludes the possibility of determining the freedom of rotation in this compound by electron diffraction. The quantitative comparison of the photographs with the 113°30′ curve having symmetry C_3 is given in Table I. The curves for the models having symmetry C_3 are shown in Fig. 2.

The two major peaks on the radial distribution curve lead to a C–C–C angle of 115°30′.

The final results are: carbon–carbon distance 1.54 ± 0.02 Å., C–C–C angle 113°30′ ± 2°. The carbon–hydrogen distance was assumed to be 1.09 Å.

***t*-Butyl Chloride.**—The *t*-butyl chloride was prepared by shaking together for fifteen minutes

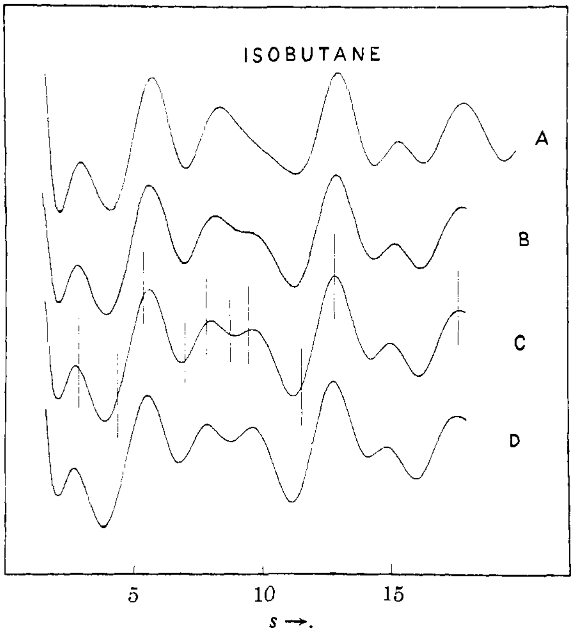


Fig. 2.—Theoretical intensity curves for isobutane. Denoting the C–C–C angle by α, curve A is calculated for α = 109°28′; curve B, α = 112°; curve C, α = 113°30′; curve D, α = 115°.

one mole of *t*-butyl alcohol and three moles of C. P. hydrochloric acid. The upper layer was recovered, washed with sodium bicarbonate solution, washed with water and fractionally distilled from calcium chloride with a three foot (91-cm.) column on which the reflux ratio could be controlled.

The photographs were taken with the sample at a temperature of 0°. Seven maxima were obtained. The first six are evenly spaced. The minimum before the fourth is somewhat less well defined than the other minima. The interval between the sixth and seventh maxima is greater than the other intervals. The seventh maximum is broad.

As in isobutane the carbon–hydrogen bonds are assumed to be at tetrahedral angles and to have an interatomic distance of 1.09 Å. Two parameters are necessary to determine the shape of the molecule—the C–C–C angle, α, and the ratio of the carbon–chlorine distance to the carbon–carbon distance, ρ. Seven theoretical intensity curves were calculated varying α from 109°28′ to 115° and varying ρ from 1.68/1.54 to 1.84/1.54. Five of these are shown in Fig. 3. In view of the large steric repulsion of the chlorine atom for the hydrogen atom, discussed above, the methyl groups are assumed to be oriented so that, for a given C–C–C angle, the hydrogen atoms are as far as possible from the chlorine atom. This orientation of the methyl groups gives the molecule the symmetry C_{3v}. All carbon–hydrogen and chlorine–hydrogen terms are included in the calculation. Models having ρ less than 1.72/1.54 are qualitatively unsatisfactory because the sixth maximum on the calculated curve is too low. When ρ is less than 1.76/1.54 α cannot be greater than 115° because the calculated fourth maximum is not sufficiently prominent. The model α equals 109°28′ and ρ equals 1.84/1.54 cannot be eliminated from a qualitative comparison with photographs but on quantitative comparison leads to a value for the carbon–carbon distance of 1.49 Å. In view of the large number of compounds in which the carbon–carbon single bond distance is observed to be 1.54 Å. this model is discarded. This procedure amounts to assum-

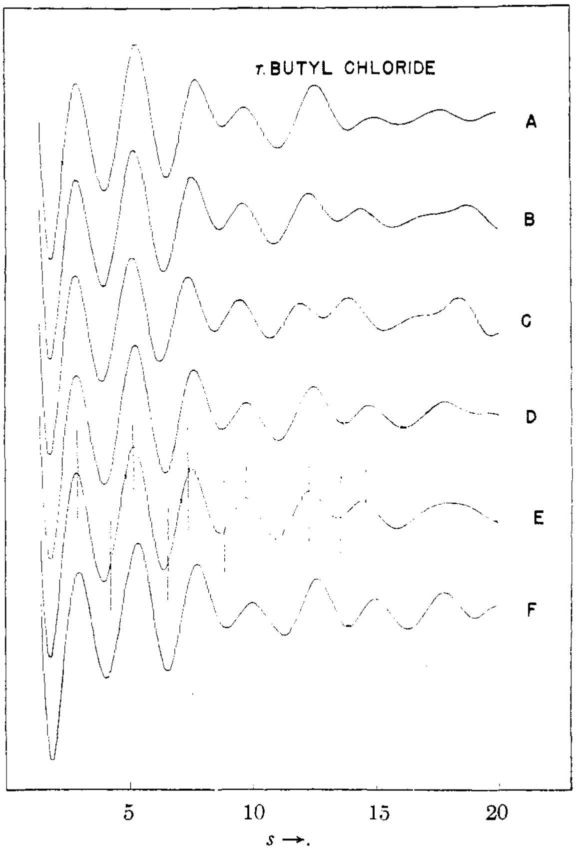


Fig. 3.—Theoretical intensity curves for *t*-butyl chloride. Denoting the C–C–C angle by α and the ratio of the C–Cl distance to the C–C distance by ρ; curve A, α = 109°28′ and ρ = 1.68/1.54; curve B, α = 109°28′ and ρ = 1.76/1.54; curve C, α = 109°28′ and ρ = 1.84/1.54; curve D, α = 112° and ρ = 1.76/1.54; curve E, α = 112° and ρ = 1.80/1.54; curve F, α = 115° and ρ = 1.76/1.54.

ing the value 1.54 Å. for the carbon–carbon distance in this compound. The most satisfactory curve is curve E for which α is 112° and ρ is 1.80/1.54. Quantitative comparison of curve E with the photographs is made in Table II.

The final results are: carbon–carbon distance 1.78 ± 0.03 Å., C–C–C angle 111°30′ ± 2°. The final result for the carbon–chlorine distance is not the 1.79 Å. obtained from curve E because quantitative comparison with curve B (less satisfactory qualitatively) gives 1.75 Å.

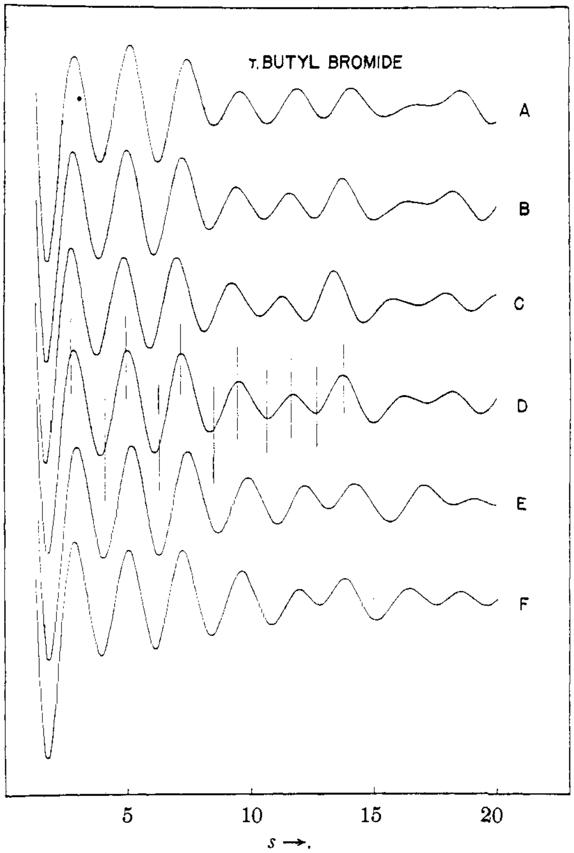


Fig. 4.—Theoretical intensity curves for *t*-butyl bromide. Denoting the C–C–C angle by α and the ratio of the C–Br distance to the C–C distance by ρ: curve A, α = 109° 28′ and ρ = 1.83/1.54; curve B, α = 109°28′ and ρ = 1.91/1.54; curve C, α = 109°28′ and ρ = 1.99/1.54; curve D, α = 112° and ρ = 1.95/1.54; curve E, α = 115° and ρ = 1.91/1.54; curve F, α = 115° and ρ = 1.99/1.54.

The six term radial distribution function is plotted in Fig. 1. It shows a strong peak at 2.74 Å. representing the long carbon–chlorine distance displaced outward slightly by some unresolved carbon–hydrogen and chlorine–hydrogen distances.

Table II

t-Butyl Chloride

Maximum	Minimum	*I*	$s_{\text{obsd.}}$	$s_{\text{calcd.}}$	C–Cl, Å.
1		25	2.887	2.86	1.784
	2		4.228	3.97	1.690
2		30	5.139	5.21	1.825
	3		6.565	6.39	1.751
3		25	7.351	7.53	1.844
	4		8.852	8.67	1.762
4		15	9.688	9.70	1.802
	5		11.22	10.95	1.757
5		10	12.12	12.31	1.829
	6		13.51	13.43	1.789
6		5	14.55	14.40	1.782
Average (1, 2 max., 2 min. omitted)					1.789

Final results: C_I–Cl 1.78 ± 0.03 Å.
C_{II}–Cl 2.69 ± 0.03 Å.
C–C–C angle 111°30′ ± 2°
C–C 1.54 Å. (assumed)
C–H 1.09 Å. (assumed)

***t*-Butyl Bromide.**—The *t*-butyl bromide was distilled from a mixture of one mole of *t*-butyl alcohol and two moles of constant boiling hydrobromic acid. It was purified in the same manner as the *t*-butyl chloride except that it was distilled from calcium bromide.

The photographs show eight evenly spaced maxima. The intensities drop off regularly except that the fifth maximum is much weaker than the sixth. The exposures were made with the sample at 25°.

The theoretical intensity curves were calculated in the same way as the chloride curves. 1.09 Å. was assumed for the carbon–hydrogen distance and models leading to values for the carbon–carbon distance much different from 1.54 Å. were discarded. Denoting the C–C–C angle by α and the ratio of the carbon–bromine distance to the carbon–carbon distance by ρ six curves were calculated varying α from 109°28′ to 115° and varying ρ from 1.83/1.54 to 1.99/1.54. These curves are shown in Fig. 4. Curves A, E and F are eliminated by the high fifth maximum. Curve C is eliminated because of the low value it gives for the carbon–carbon distance. Of the remaining two curves, curve D is the most satisfactory. Quantitative comparison of the photographs with this curve is made in Table III. The quantitative comparison with curve B is allowed to influence the curve D result in obtaining the final results. The final results are: carbon–bromine distance 1.92 ± 0.03 Å., C–C–C angle 111°30′ ± 2°.

Dornte[7] reported a C–C–C angle of 110° and a C–Br distance of 2.06 Å. for this compound. We regard his interpretation as less reliable than ours because his photographs showed fewer maxima and minima than ours and also because he considered only one molecular model (omitting all carbon–hydrogen and bromine hydrogen terms) in making his interpretation.

TABLE III

t-BUTYL BROMIDE

Maximum	Minimum	I	$s_{\text{obsd.}}$	$s_{\text{calcd.}}$	C–Br, Å.
	1		1.856	1.72	1.808
1		20	2.737	2.80	1.995
	2		4.113	3.86	1.829
2		20	4.959	4.97	1.954
	3		6.320	6.07	1.872
3		15	7.176	7.18	1.952
	4		8.522	8.32	1.903
4		11	9.463	9.48	1.954
	5		10.719	10.67	1.940
5		3	11.624	11.69	1.962
	6		12.770	12.60	1.925
6		7	13.751	13.71	1.944
Average (1, 2 min., 1 max. omitted)					1.934

Final results: C_I–Br 1.92 ± 0.03 Å.
C_{II}–Br 2.79 ± 0.03 Å.
C–C–C angle 111° 30′ ± 2°
C–C 1.54 Å. (assumed)
C–H 1.09 Å. (assumed)

The six term radial distribution function, plotted in Fig. 1, shows a large peak at 2.82 Å. This represents the long carbon–bromine distance and some unresolved less important distances.

We wish to express our appreciation to Professor C. P. Smyth for suggesting that the apparatus be built and for his continued interest in the research.

Summary

The molecular structures of isobutane, *t*-butyl chloride and *t*-butyl bromide have been determined by electron diffraction. The C–C–C angles are 113°30′ ± 2°, 111°30′ ± 2° and 111°30′ ± 2° for isobutane, *t*-butyl chloride and *t*-butyl bromide, respectively. The interatomic distances are C–C 1.54 ± 0.02 Å., C–Cl 1.78 ± 0.03 Å. and C–Br 1.92 ± 0.03 Å.

The steric repulsions between hydrogen and halogen are calculated and compared with the electrostatic interactions.

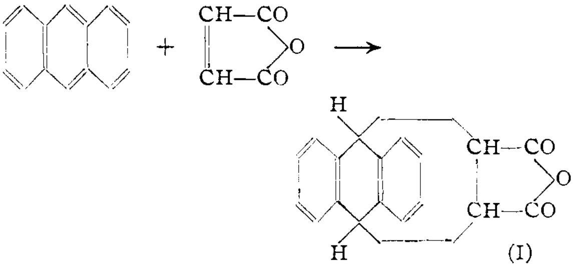
PRINCETON, N. J. RECEIVED DECEMBER 4, 1937

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

The Reaction between Maleic Anhydride and Polycyclic Hydrocarbons

BY W. E. BACHMANN AND M. C. KLOETZEL[1]

Diels and Alder[2] prepared anthracene-9,10-*endo*-α,β-succinic anhydride (I) by fusing a mixture of anthracene and maleic anhydride just below 260°.



(I)

Clar[3] obtained the adduct by heating a solution of the two compounds in xylene and used this procedure to prepare the adducts of a number of polycyclic hydrocarbons with maleic anhydride. Other investigators have employed either the fusion method or the reaction in a solvent, usually a high-boiling liquid such as xylene, *o*-dichlorobenzene or nitrobenzene. Although the yields of the adducts were not always satisfactory, no systematic study has been made on any of the polycyclic hydrocarbons to determine the conditions for securing the maximum yields of the adducts. The necessity of some such study was brought to our attention in attempting to prepare the adduct (II) from maleic anhydride and 3-methylcholanthrene.

On heating a mixture of equimolecular proportions of maleic anhydride and 3-methylcholanthrene in xylene at the boiling point of the solution for two hours a 22% yield of the adduct (II) was obtained. In an attempt to improve the yield, we resorted to a higher temperature, using anisole and nitrobenzene as solvents and carrying out the reactions at the boiling points of the solutions, but the yields of the adduct were found to

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(1) Du Pont Post-Doctorate Fellow.

(2) Diels and Alder, *Ann.*, **486**, 191 (1931).

(3) Clar, *Ber.*, **64**, 2194 (1931).