equation of the straight line representing these data, obtained by the method of least squares, is

$$C_p^0 = 3.32 + 0.516T$$

The values obtained with this equation are given in the last column of Table II.

By comparison of the results attained with air and *n*-butane with the apparatus and technique employed, it is believed that the over-all accuracy of the 1,3-butadiene heat capacities is better than 1 part in 100.

Acknowledgment.—The authors wish to thank Dr. C. S. Cragoe of the National Bureau of Standards for his interest in the problem and for his efforts in securing the sample of butadiene. They also wish to thank the Phillips Petroleum Company of Bartlesville, Oklahoma, for the liberal sample of highly purified butadiene used in this investigation.

Summary

1. The heat capacities of *n*-butane and of air were determined, for calibration purposes, at 25°.

2. Six values of the molar heat capacities of 1,3-butadiene were determined over the range 5 to 105°.

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The Crystal Structure of Biphenylene

BY JURG WASER AND CHIA-SI LU

In an earlier paper,[1] which reported on the electron diffraction of biphenylene molecules, $C_{12}H_8$, the configuration of the carbon atoms in these molecules, as suggested by Lothrop's synthesis,[2] was confirmed, and values for various interatomic distances were assigned. In addition resonance energy and bond strengths were calculated. The present investigation deals with the crystal structure of biphenylene, and provides further proof that the compound investigated is indeed dibenzcyclobutadiene.

Unit Cell and Space Group

It was found that sublimation of biphenylene under controlled conditions resulted in sharp needles, which were, however, much too thin for X-ray work. Recrystallization from *n*-propyl alcohol gave satisfactory crystals. They were prisms, 0.25–0.5 mm. thick and 2–3 mm. long, with side faces belonging predominantly to the forms {110}, {310}, {100} and {010}. The straw-colored crystals had no distinct cleavage and showed no abnormal birefringence. Due to their appreciable vapor pressure at room temperature, their faces disappeared within a few hours on standing in open air, and the crystals evaporated completely within a few days.

All X-ray photographs showed a rather large temperature factor. Rotation and Weissenberg photographs about the three crystallographic axes led to the following dimensions of the monoclinic unit cell: $a_0 = 19.60 \pm 0.03$ Å., $b_0 = 10.50 \pm 0.02$ Å., $c_0 = 5.84 \pm 0.02$ Å., $\beta = 91°20' \pm 20'$. The absence of $(h0l)$ reflections with odd h and of $(0k0)$ reflections with odd k indicates $C_{2h}^5 - P2_1/a$ as the probable space group. Rough density measurements by flotation in an aqueous solution of potassium iodide gave $\rho = 1.24$ g./cc. Hence there are six molecules per unit cell, the calculated density being $\rho = 1.25$ g./cc.

Intensities of $(hk0)$ and $(h0l)$ reflections were estimated from Weissenberg photographs taken with unfiltered Cu K radiation, using the multiple film technique.[3] The specimens chosen for diffraction work were small enough to make absorption corrections unnecessary. It was very difficult to obtain satisfactory visual intensity correlations between different $(h0l)$ reflections due to their varying sizes, as for these reflections the axis of rotation of the crystal was perpendicular to the needle axis. It was not possible to cut a crystal sufficiently short so that its length would approximate its thickness Since there is no similar difficulty for $(hk0)$ reflections, the intensity values obtained for them should be much more reliable than the ones for $(h0l)$ reflections. No quantitative intensity data for $(0kl)$ reflections were collected, since a Fourier projection along the a axis was not expected to show any resolution.

The relative intensities obtained were corrected for the Lorentz and polarization factors with Lu's chart[4] and the scale of their square roots was adjusted to approximately absolute scale by comparison with the values calculated from the final structure. These experimental structure factors are recorded in the second columns of Tables I and II in the order of decreasing spacing, except that the values for $(h0\bar{l})$ and $(h0l)$ have been grouped together.

Determination of the Structure

In the space group $C_{2h}^5 - P2_1/a$ there are four sets of two-fold positions with the point symmetry

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[1] J. Waser and V. Schomaker, THIS JOURNAL, **65**, 1451 (1943).

[2] W. C. Lothrop, *ibid.*, **63**, 1187 (1941); **64**, 1698 (1942).

[3] J. J. De Lange, J. M. Robertson and I. Woodward, *Proc. Roy. Soc.* (London), **A171**, 398 (1939).

[4] C. S. Lu, *Rev. Sci. Inst.*, **14**, 331 (1943).

TABLE I

$(hk0)$	$\lvert F_{\text{obs.}}\rvert$	$F^{(1)}_{\text{calcd.}}$	$(hk0)$	$\lvert F_{\text{obs.}}\rvert$	$F^{(1)}_{\text{calcd.}}$	$(hk0)$	$\lvert F_{\text{obs.}}\rvert$	$F^{(1)}_{\text{calcd.}}$
301	34	40	970	0	−8	21.4.0	0	4
020	51	87	15.3.0	22	−22	0.12.0	21	29
320	62	99	680	0	−4	9.11.0	0	4
600	37	−34	12.6.0	19	22	15.9.0	0	−2
610	38	−37	15.4.0	0	−8	3.12.0	0	2
330	50	69	390	0	5	21.5.0	0	−6
620	0	7	980	20	−21	6.12.0	0	−7
040	11	11	15.5.0	0	4	18.8.0	0	1
340	19	−23	12.7.0	0	−7	12.11.0	0	−5
630	0	−2	690	0	1	21.6.0	0	−1
910	0	4	18.0.0	35	−39	15.10.0	0	−5
640	0	−8	18.1.0	14	14	24.0.0	10	15
920	31	31	18.2.0	16	−14	24.1.0	0	−1
350	23	13	0.10.0	14	22	9.12.0	0	−1
930	35	−20	15.6.0	0	0	24.2.0	0	−2
650	32	14	18.3.0	0	4	3.13.0	0	9
060	41	40	3.10.0	33	−24	18.9.0	0	−7
360	0	1	990	0	−2	24.3.0	0	−3
940	29	27	12.8.0	0	9	21.7.0	0	−3
12.0.0	30	−25	18.4.0	0	−6			
12.1.0	0	−4	6.10.0	0	−2			
12.2.0	15	−6	15.7.0	0	2			
660	32	−32	18.5.0	9	−6			
950	15	−10	12.9.0	0	−5			
12.3.0	13	9	9.10.0	12	−11			
370	0	8	3.11.0	0	−2	$\lvert F_{hk0}\rvert$ observed for $h \neq 3n$[a])		
12.4.0	16	16	21.1.0	21	−19			
960	0	−1	15.8.0	0	4			
670	0	−8	18.6.0	11	−12			
080	0	−8	21.2.0	18	−19	220	7	
15.1.0	0	0	6.11.0	0	−11	230	9	
12.5.0	12	8	21.3.0	8	−5	420	5	
380	0	−5	12.10.0	0	−6	520	6	
15.2.0	0	1	18.7.0	0	3	530	6	

[a] *Cf.* also Table II.

TABLE II

$(h0l)$	$\lvert F_{\text{obs.}}\rvert$	$F^{(1)}_{\text{calcd.}}$	$F^{(2)}_{\text{calcd.}}$	$(h0l)$	$\lvert F_{\text{obs.}}\rvert$	$F^{(1)}_{\text{calcd.}}$	$F^{(2)}_{\text{calcd.}}$
200	5	0	3	$60\bar{5}$	7	8	9
001	26	−28	−31	605	8	6	11
$20\bar{1}$	6	2	−5	18.0.0	35	−39	−31
201	37	44	47	$12.0.\bar{4}$	8	7	8
400	5	0	1*	12.0.4	4	−9	−6
$40\bar{1}$	18	27	19	$18.0.\bar{1}$	13	−11	−13
401	19	15	14	18.0.1	32	20	25
600	37	−34	−40	$80\bar{5}$	14	10	11
002	0	1	0	805	4	−6	−5
$60\bar{1}$	26	29	23	$16.0.\bar{3}$	9	3	6
601	32	−33	−33	16.0.3	4	−8	−5
$20\bar{2}$	10	13	9	$18.0.\bar{2}$	0	−4	−5
202	38	−32	−34	18.0.2	5	−3	−5
$40\bar{2}$	42	23	32	$14.0.\bar{4}$	9	−4	−8
402	13	18	12	14.0.4	13	−11	−16
800	0	0	0	$10.0.\bar{5}$	0	1	3
$80\bar{1}$	0	0	0	10.0.5	7	−9	−8
801	3	4	7	20.0.0	7	0	−5
$60\bar{2}$	11	4	5	006	0	−8	0
602	8	1	6	$20\bar{6}$	0	1	0
10.0.0	6	0	1*	206	0	−2	−2
003	5	8	8	$20.0.\bar{1}$	3	−5	−4
$20\bar{3}$	13	12	16	20.0.1	7	−12	−10
203	11	15	12	$40\bar{6}$	5	4	6
$80\bar{2}$	5	−10	−6	406	5	3	7
802	44	42	38	$18.0.\bar{3}$	0	0	0
$10.0.\bar{1}$	5	2	−10	18.0.3	0	−2	1
10.0.1	6	8	18	$12.0.\bar{5}$	0	4	3
$40\bar{3}$	34	−25	−31	12.0.5	3	5	5
403	28	−20	−23	$16.0.\bar{4}$	0	2	1
$60\bar{3}$	0	0	−2	16.0.4	0	−2	1
603	17	−12	−14	$60\bar{6}$	0	1	1
12.0.0	30	−25	−27	606	0	0	−1
$10.0.\bar{2}$	43	−41	−33	$20.0.\bar{2}$	0	1	2
10.0.2	4	2	−6*	20.0.2	3	1	1
$12.0.\bar{1}$	7	6	2	$80\bar{6}$	4	−1	−4
12.0.1	6	−1	4	806	4	−2	−3
$80\bar{3}$	7	−5	−7	$14.0.\bar{5}$	9	10	12
803	15	−14	−12	14.0.5	4	−7	−5
004	0	0	0	22.0.0	3	0	1
$20\bar{4}$	13	−7	−9	$22.0.\bar{1}$	0	−6	−4
204	13	7	13	22.0.1	0	−6	−1
$12.0.\bar{2}$	0	5	1	$20.0.\bar{3}$	6	−2	−2
12.0.2	4	3	0	20.0.3	6	−8	−8
14.0.0	0	0	−2	$18.0.\bar{4}$	11	−5	−11
404	12	7	9	18.0.4	4	7	9
$40\bar{4}$	10	12	8	$10.0.\bar{6}$	0	2	1
$10.0.\bar{3}$	0	7	7	10.0.6	0	1	0
10.0.3	7	13	10	$22.0.\bar{2}$	5	−4	−5
$14.0.\bar{1}$	3	0	4	22.0.2	0	−1	3
14.0.1	14	−8	−10	$16.0.\bar{5}$	0	−4	−1
$60\bar{4}$	23	17	22	16.0.5	4	−8	−6
604	18	−18	−19	$12.0.\bar{6}$	5	6	5
$14.0.\bar{2}$	8	−4	−6	12.0.6	5	−1	−5
14.0.2	3	−9	−7	007	3	6	−1*
$80\bar{4}$	9	−14	−8	$20\bar{7}$	0	1	1
804	17	−7	−12	207	2	−1	0*
$12.0.\bar{3}$	0	2	3	$40\bar{7}$	3	1	−3
12.0.3	0	3	0	407	0	0	2
16.0.0	0	0	0	24.0.0	10	15	14
$16.0.\bar{1}$	13	−11	−12	$20.0.\bar{4}$	10	9	9
16.0.1	12	−1	−8	20.0.4	4	2	5
$10.0.\bar{4}$	0	−5	−8	$22.0.\bar{3}$	0	1	0
10.0.4	0	−1	8	22.0.3	3	6	5
005	27	−26	−32	$24.0.\bar{1}$	2	2	6
$20\bar{5}$	23	27	22	24.0.1	5	−3	−6
205	6	−6	−7	$60\bar{7}$	4	4	7
$14.0.\bar{3}$	7	6	7	607	4	9	4
14.0.3	11	15	15	$14.0.\bar{6}$	0	−1	0
$40\bar{5}$	17	15	16	14.0.6	0	−1	1
405	30	−31	−32	$18.0.\bar{5}$	5	3	4
$16.0.\bar{2}$	14	16	14	18.0.5	3	10	6
16.0.2	11	−10	−9	$80\bar{7}$	0	4	4
				807	0	−7	−6

* Omitted in calculation of $\rho(x,z)$.

C_i: 000, $\frac{1}{2}\frac{1}{2}0$; $\frac{1}{2}00$, $0\frac{1}{2}0$; $00\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; and $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$; and sets of four-fold general positions: $\pm(xyz, \frac{1}{2} + x\frac{1}{2} - yz)$. As there are six molecules in the unit cell, at least two must have centers of symmetry with these centers placed in the set of two-fold special positions. The special positions 000, $\frac{1}{2}\frac{1}{2}0$ may be chosen without loss of generality. The considerations of the next paragraph rule out special positions for the other four molecules, which accordingly are placed in the set of general positions. All atoms will thus in general occupy four-fold positions.

The reflections $(hk0)$ show a very distinctive feature. Except for a few, all of which are very weak, only reflections $(hk0)$ with $h = 3n$ appear. The reflections $(h0l)$ show no similar regularity. Assuming in a first approximation that all reflections $(hk0)$ vanish unless $h = 3n$ ("$h = 3n$ rule"), atoms have to be grouped in triplets, the partner in each triplet occupying the following set of positions: xyz_1, $x + \frac{1}{3}\, yz_2$, $x + \frac{2}{3}\, yz_3$. The part of the structure factor due to each triplet then becomes zero unless $h = 3n$.

The seventy-two carbon atoms (and the forty-eight hydrogen atoms, which, however, will be neglected) thus fall into groups of twelve atoms, the positions of which are interrelated either by space-group operations or by the requirements of the "$h = 3n$ rule." The coördinates of such a set of positions are: $x_1\ y_1\ z_1$, $\bar{x}_1\ \bar{y}_1\ \bar{z}_1$; $\frac{1}{2} + x_1\ \frac{1}{2} - y_1\ z_1$, $\frac{1}{2} - x_1\ \frac{1}{2} + y_1\ \bar{z}_1$; $\frac{1}{3} + x_1\ y_1\ r + z_1'$,

$\frac{1}{3} - x_1\ \bar{y}_1\ r - z_1'$; $\frac{2}{3} + x_1\ y_1\ \bar{r} + z_1'$, $\frac{2}{3} - x_1\ \bar{y}_1\ \bar{r} - z_1'$; $\frac{1}{6} + x_1\ \frac{1}{2} - y_1\ \bar{r} + z_1'$, $\frac{1}{6} - x_1\ \frac{1}{2} + y_1\ \bar{r} - z_1'$; $\frac{5}{6} + x_1\ \frac{1}{2} - y_1\ r + z_1'$, $\frac{5}{6} - x_1\ \frac{1}{2} + y_1\ r - z_1'$, with $r = \frac{1}{2}(z_2 - z_3)$, $z_1' = \frac{1}{2}(z_2 + z_3)$. These positions can be grouped, as has been done above, into pairs about six centers of symmetry with the parameters 000, $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{3}\ 0\ r$, $\frac{2}{3}\ 0\ \bar{r}$, $\frac{1}{6}\ \frac{1}{2}\ \bar{r}$, $\frac{5}{6}\ \frac{1}{2}\ r$. Since the magnitudes of the x parameters and of the y parameters relative to these centers are, respectively, the same, these centers must be the centers of the six molecules in the unit cell. Assuming that the molecules in the general positions have the same size and shape as the ones in the special position, there are two possibilities left to relate z_1' with z_1: (a) the molecules at 000 and $\frac{1}{3}\ 0\ r$ are parallel to each other, thus $z_1' = z_1$; (b) the orientation of the molecule at $\frac{1}{3}\ 0\ r$ results from the orientation of the molecule at 000 by a mirror operation by a plane perpendicular to the c axis. Then $z_1' \approx -z_1$, since the c axis is almost perpendicular to the a axis.

In the present approximation the orientations of all six molecules are interrelated. This makes possible the application of the method of the molecular structure factor.[5] In this method, the size and the shape of the molecule are assumed and its Fourier transform is constructed. If the orientations of all molecules in the unit cell are interrelated, then the molecular structure factors, read off from a chart of the Fourier transform, are related to the structure factors of the whole unit cell. The problem is then to orient the reciprocal lattice of the crystal with respect to the system of axes of the Fourier transform in such a way as to account for the observed structure factors.

In the case of biphenylene the Fourier transform has an especially useful form. Since the molecule may be assumed to have a center of symmetry and to be planar, the transform is real and essentially two-dimensional. The model chosen for the calculation was suggested by the electron diffraction investigation.[1] It consists of two regular ($\alpha = 120°$) coplanar hexagons of carbon atoms with bond lengths $a = 1.40$ Å., joined by two bridges, in ortho positions, of lengths $b = 1.46$ Å. (Fig. 1). The use of the Fourier transform reduces the original fifty-four parameter problem, involving the placement of eighteen carbon atoms, to a four parameter problem, in which three parameters characterize the orientation of the molecule and the fourth one is the parameter r.

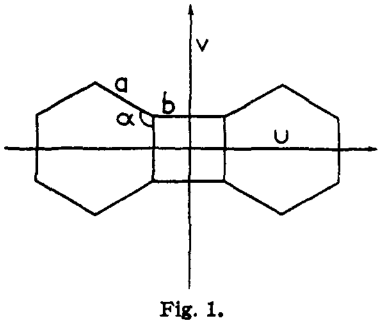

Fig. 1.

Reflections ($hk0$) are especially suited to determine the orientation of the molecules since in this case the relationship between molecular and crystal structure factors does not involve the parameter r, and does not distinguish between the possibilities (a) and (b). After a few trials, general agreement between calculated and observed structure factors was obtained, resulting in the determination of most of the phase constants. These phase constants combined with the observed structure factors were used in the calculation of the Fourier projection

$$\rho(x,y) = C\sum_h\sum_k F_{hk0} \cos 2\pi(hx + ky)$$

This calculation was carried out with use of Lipson–Beevers strips[6] at intervals of $a_0/180$ and $b_0/60$. The plot of the final projection obtained with the signs calculated from the final choice of parameters (Table III, assignment No. 1) is shown in Fig. 2. Due to the approximation involved, the length of the a axis of the unit cell of the projection is equal to $\frac{1}{3}a_0$, and the projection shown corresponds to a superposition of the molecules at 000, $\frac{1}{3}\ 0\ r$, $\frac{2}{3}\ 0\ \bar{r}$. Figure 3 shows the actual unit cell of the crystal viewed along the c axis and its relation to Fig. 2.

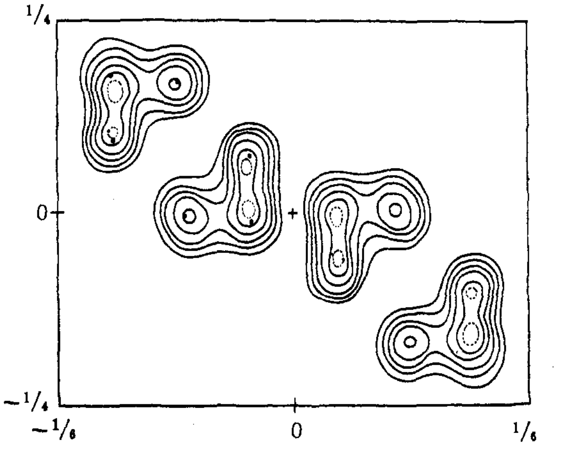

Fig. 2.—Fourier projection $\rho(x,y)$. Dots (●) indicate parameters of assignment No. 1.

The knowledge of the approximate orientations of the molecules and the observed values of $|F_{h0l}|$ were used with the Fourier transform to decide between the alternatives (a) and (b) and to determine the parameter r. It was found that the arrangement (a) could not account for the observed ($h0l$) intensities. For testing the arrangement (b) it proved helpful to determine the probable range of the parameter r in the following manner. Paper models of the xz projections of the molecules were constructed to scale

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(5) G. Knott, *Proc. Phys. Soc.* (London), **52**, 229 (1940).

(6) H. Lipson and C. A. Beevers, *ibid.*, **48**, 772 (1936).

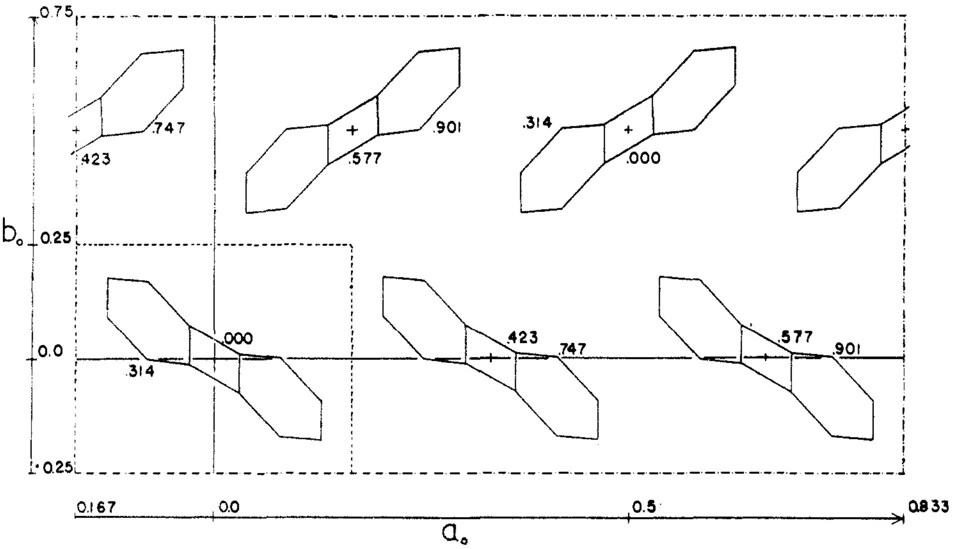

Fig. 3.—View of xy projection of unit cell of crystal (parameter assignment No. 1). Numbers given to three decimal places are z parameters of center and of highest atom for each molecule. Section enclosed within broken lines indicates area represented in Fig. 2.

and manipulated over a plot of several unit cells. The packing was tested for each value of r chosen by estimating the intramolecular distances. General agreement between observed structure factors and the values calculated from the Fourier transform was obtained for $r = 0.43$, which was in the expected range. The signs of the F_{h0l} obtained in this manner were combined with the experimental $|F_{h0l}|$ and a Fourier projection

$$\rho(x,z) = c\sum_h\sum_l F_{h0l}\cos 2\pi(hx + lz)$$

was calculated. The summations involved were evaluated with the aid of International Business Machine Corporation machines and a set of punched cards,[7] sixty-six lines parallel to the c axis and eighty-six lines parallel to the a axis being chosen. Figure 4 shows a plot of $\rho(x,z)$ obtained with the final choice of signs explained later. Twenty-six of the thirty-one peaks are resolved, although not all completely. The x parameters of the various resolved peaks agree well with the x parameters of the peaks in $\rho(x,y)$ (Fig. 2). Figure 5, a diagram of two unit cells of the crystal viewed along the b axis, explains the relationship between the peaks of $\rho(x,z)$.

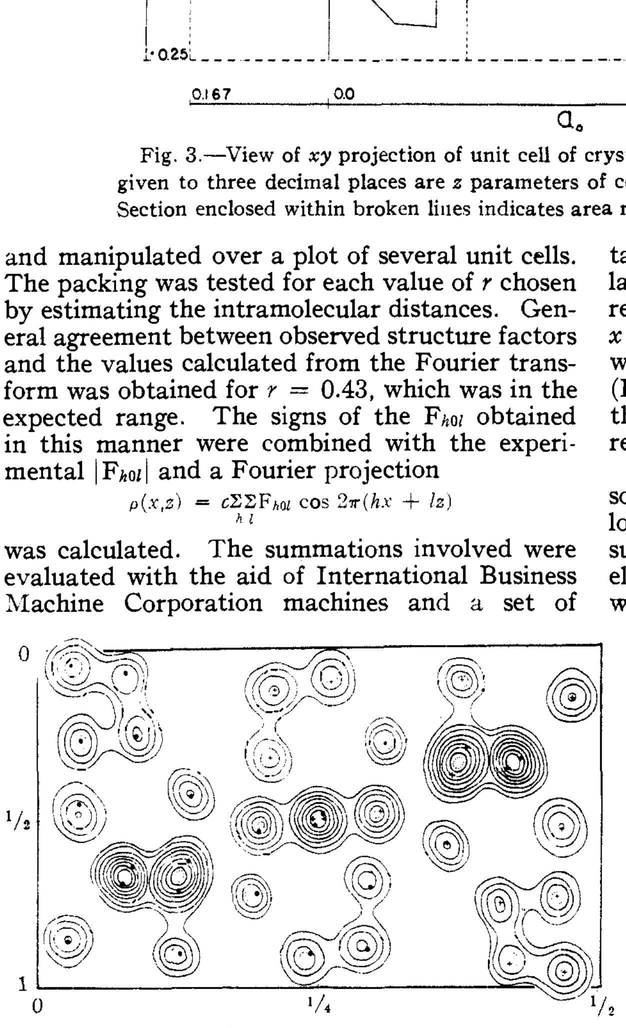

Fig. 4.—Fourier projection $\rho(x,z)$. Black dots (●) indicate parameters of assignment No. 1; crosses (+) represent parameters of assignment No. 2.

An interpretation of the peaks of $\rho(x,z)$ was sought in the following manner. The two crystallographically different kinds of molecules were assumed to have the dimensions suggested by the electron diffraction work,[1] a coplanar molecule with $a = 1.40$ Å., $\alpha = 121°$, and $b = 1.46$ Å. (Fig. 1). The orientations of the molecules relative to each other, and the parameters of the centers of the molecules in the general positions (pqr and space group equivalents) were chosen so as to agree with the requirements of the "$h = 3n$ rule" ($p = \frac{1}{3}$; $q = 0$). Parameter values for all carbon atoms were then found by matching these molecules (by trial and error), as closely as possible to the maxima of $\rho(x,y)$ and of $\rho(x,z)$. The final choice for the parameters is recorded in Table III (Assignment No. 1) and dots in Figs. 2 and 4 indicate their positions with respect to the maxima of $\rho(x,y)$ and of $\rho(x,z)$. Figures 3 and 5 were drawn with these parameters, which were also used for the calculation of structure factors $F^{(1)}_{hk0}$ and $F^{(1)}_{h0l}$. These structure factors are recorded in the third columns of Tables I and II. Robertson's atomic scattering factors for hydrocarbons[8] were used in these calculations. The agreement between $|F_{\text{calcd.}}|$ and $|F_{\text{obs.}}|$ is reasonably good, but not entirely satisfactory. Attempts to orient the molecules in the

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(7) P. A. Shaffer, Jr., Ph.D. Thesis, California Institute of Technology, 1942.

(8) J. M. Robertson, *Proc. Roy. Soc.* (London), **A150**, 106 (1935).

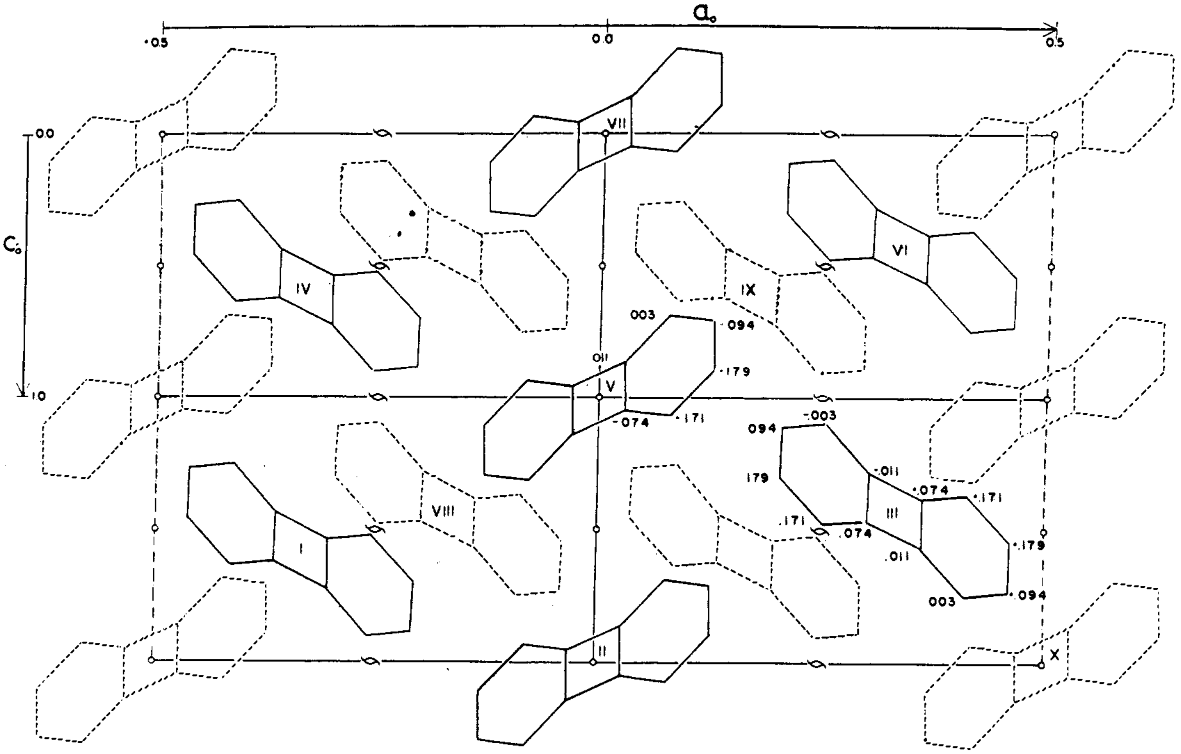

Fig. 5.—Two unit cells of crystal viewed along *b* axis are shown (parameter assignment No. 1). Numbers given to three decimal places are *y* parameters of carbon atoms. Molecules drawn with solid lines have centers at $y = 0$, those drawn with broken lines have centers at $y = {}^1/_2$.

general positions in a different way (abandoning the "$h = 3n$ rule") failed to give improvement.

TABLE III

Parameters

	Assignment No. 1			Assignment No. 2		
	u	*v*	*w*	*u*	*v*	*w*
Molecule with center at (000):	0.029	0.011	−0.140	0.029	(−0.003)	−0.147
	.077	.003	− .314	.073	(− .026)	− .319
	.127	− .094	− .294	.122	(− .119)	− .294
	.128	− .179	− .107	.126	(− .189)	− .097
	.080	− .171	.067	.082	(− .166)	+ .075
	.030	− .074	.047	.033	(− .073)	.050
	.363	− .074	.380	.366	(− .069)	.370
	.413	− .171	.367	.416	(− .161)	.348
	.461	− .179	.547	.463	(− .183)	.526
	.460	− .094	.734	.460	(− .111)	.724
	.410	.003	.747	.410	(− .019)	.746
Molecule with center at (*pqr*):	.362	.011	.567	.363	(.003)	.568
	.304	− .011	.279	.308	(− .003)	.278
	.256	− .003	.099	.261	(.019)	.100
	.206	.094	.112	.211	(.111)	.122
	.205	.179	.299	.208	(.183)	.320
	.253	.171	.479	.255	(.161)	.498
	.303	.074	.466	.305	(.069)	.476
Center (*pqr*):	.333	.000	.423	.335₅	(.000)	.423

In principle the projection $\rho(x,z)$ can be used to discard the "$h = 3n$ rule." The reasonable assumption could be made that the molecules have the symmetry D$_{2h}$-mmm. The molecules in the general positions would have their centers at *pqr* and corresponding positions (with $p \approx \frac{1}{3}$, $q \approx 0$), and in general would have size and shape different from the molecule with center at 000. Parameters *xyz* could be determined (except for the small additional constant *q* in the parameters *y*) by a least-squares fit of such molecules to the maxima of $\rho(x,z)$, using the symmetry conditions as auxiliary conditions. These parameters could then be used to determine the signs of *all* F_{hk0} and a complete projection $\rho(x,y)$ could be constructed.

An attempt to obtain refinement along these lines was made. For simplicity, it was further assumed that the six-rings of biphenylene (Fig. 1) are regular hexagons. Although these assumptions are probably not strictly valid, they can be used as a basis for a second approximation. The two kinds of biphenylene molecules were fitted to the maxima of $\rho(x,z)$ by trial and error, rather than by a laborious least-squares treatment. The resulting parameters are recorded in Table III (Assignment No. 2), and the crosses in Fig. 4 indicate their relationship with the peaks of $\rho(x,z)$, which they approach more closely than do the parameters of assignment No. 1. It is seen that the *y* parameters are not in good agreement with the *y* parameters of assignment No. 1 corresponding to the maxima of $\rho(x,y)$. The C–C bond distances obtained for the two kinds of molecules for assignment No. 2 do not agree well with each other nor with the electron diffraction result.[1] (The values are $a = 1.37$ Å., $b = 1.58$ Å.

for the molecule with center at 000, and a = 1.39 Å., b = 1.44 Å. for the molecule with center at pqr.) Nevertheless the parameters obtained were used to calculate a set of structure factors $F^{(2)}_{h0l}$ which are recorded in the fourth column of Table II. Some improvement over the values of $F^{(1)}_{h0l}$ is noted. The Fourier projection shown in Fig. 4 was made using the signs of the $F^{(2)}_{h0l}$ (omitting a few terms with uncertain signs), since the parameters used to calculate the $F^{(2)}_{h0l}$ correspond more closely to the maxima of $\rho(x,z)$ than do the parameters used in the calculation of the $F^{(1)}_{h0l}$. In most instances the signs of $F^{(1)}_{h0l}$ and $F^{(2)}_{h0l}$ are the same. With few exceptions $|F^{(1)}_{h0l}| \ll |F^{(2)}_{h0l}|$ whenever the signs are different, so that the signs of these $F^{(2)}_{h0l}$ are probably correct. The remaining values $F^{(2)}_{h0l}$, for which the signs are less certain, appear starred in Table II, and have been omitted from the calculation of $\rho(x,z)$ of Fig. 4. There are few of them and their magnitudes are so small that their omission is not expected to change the positions of the maxima of $\rho(x,z)$ appreciably. A Fourier projection involving all the certain phase constants of the $F^{(1)}_{h0l}$ was carried through also, but only very slight shifts in the positions of the peaks of $\rho(x,z)$ were observed. Structure factors for reflections ($0kl$) were also calculated with parameter assignment No. 1 and show qualitative agreement with intensities estimated from a Weissenberg photograph.

The improvement from $F^{(1)}_{h0l}$ to $F^{(2)}_{h0l}$ is not good enough to make parameter assignment No. 2 significant, or to suggest in which direction further improvement should be sought. The resolution of $\rho(x,z)$ is not sufficient, nor are the observed $|F_{h0l}|$ believed to be accurate enough to justify any further attempt at refinement.

Assignment No. 1 of parameters was finally adopted. It corresponds to the following orientations of the molecules at (000) and at (pqr). Let w be the direction perpendicular to u and v (Fig. 1) so that u, v, w form a right-hand system. Let x and y be the directions parallel to the a and b axes of the unit cell, respectively, and let z be directed normal to both, so that x, y, z, form a right-hand system. Then the angles between u, v, w and x, y, z are as follows

	Molecule at 000			Molecule at pqr		
	u	v	w	u	v	w
x	36.1°	90.0°	53.8°	37.6°	91.8°	127.5°
y	117.1°	50.8°	51.3°	117.1°	50.8°	128.7°
z	111.9°	140.8°	59.3°	66.1°	39.3°	60.9°

The parameters adopted are not entirely correct, since for them the "$h = 3n$ rule" holds, while experimentally there are some infractions. These may be an indication that the two molecules are not exactly of the same size and shape or that their orientations and the positions of their centers differ slightly from the ones demanded by the "$h = 3n$ rule." In addition, the general agreement between the $|F^{(1)}_{\text{calcd.}}|$ and the $|F_{\text{obs.}}|$ is by no means perfect. However, with fifty-four parameters to dispose of, it may be considered to be reasonably satisfactory. No probable errors can be given for the adopted parameters, since the reliability of the observed $|F_{h0l}|$ is not known. It is, however, likely that most atomic positions are correct to within 0.1 Å. A few may be in error by a somewhat larger amount, as is suggested by calculations of intermolecular distances.

Discussion

The results of this investigation prove beyond doubt that the substance in question is dibenzcyclobutadiene.

The parameter values are, in addition, good enough to establish the packing arrangement of the molecules in the crystal. A packing drawing (Fig. 6) of the crystal was constructed in the following manner. The proper carbon atoms were provided with hydrogen atoms at C–H distances of 1.08 Å., and in directions bisecting the corresponding C–C–C angles. Spheres with van der Waals radii[9] of 1.85 Å. for carbon (half thickness of an aromatic molecule), and of 1.20 Å. for hydrogen were drawn about the centers of the carbon and hydrogen atoms of a molecule and intersected with each other (*cf.* bottom molecule in Fig. 6). The resulting van der Waals representations of the molecules, drawn in correct orientations and positions, constitute Fig. 6, which is a view of the crystal along the b axis. Two layers of molecules are drawn in Fig. 6. The complete bottom layer is shown to illustrate the interactions within one layer. The next layer is related to the bottom layer by a glide plane a, parallel to and at a distance of $\frac{1}{4}$ b_0 from the first layer. It is represented by three molecules only, since these three suffice to illustrate the interactions between the two different layers. The next layer (not shown) is a replica of the bottom layer, translated by b_0 in the direction of the b axis.

To gain an understanding of Fig. 6 comparison with Fig. 5 will prove helpful. The space group elements indicated in Fig. 5 are useful also in finding different views of the same interaction.

The following contacts are recognized in the bottom layer of Fig. 6. Molecules forming ribbons parallel to the c_0 axis interact like II and II′ at A. There are three such ribbons per unit a_0. In two of them (R_1 and R_1') the molecules are tilted in one direction from the c axis; in the third (R_2) this tilt is in the opposite direction. Ribbons of the same kind, R_1 and R_1', interact in the following way: the benzene ring of molecule IV′ partly overlaps the benzene ring of molecule VI at B, and VI and I′ contact each other edge on at C. The interactions between the two different

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[9] L. Pauling, "The Nature of the Chemical Bond," 2nd edition, Ithaca, N. Y., 1940, p. 189.

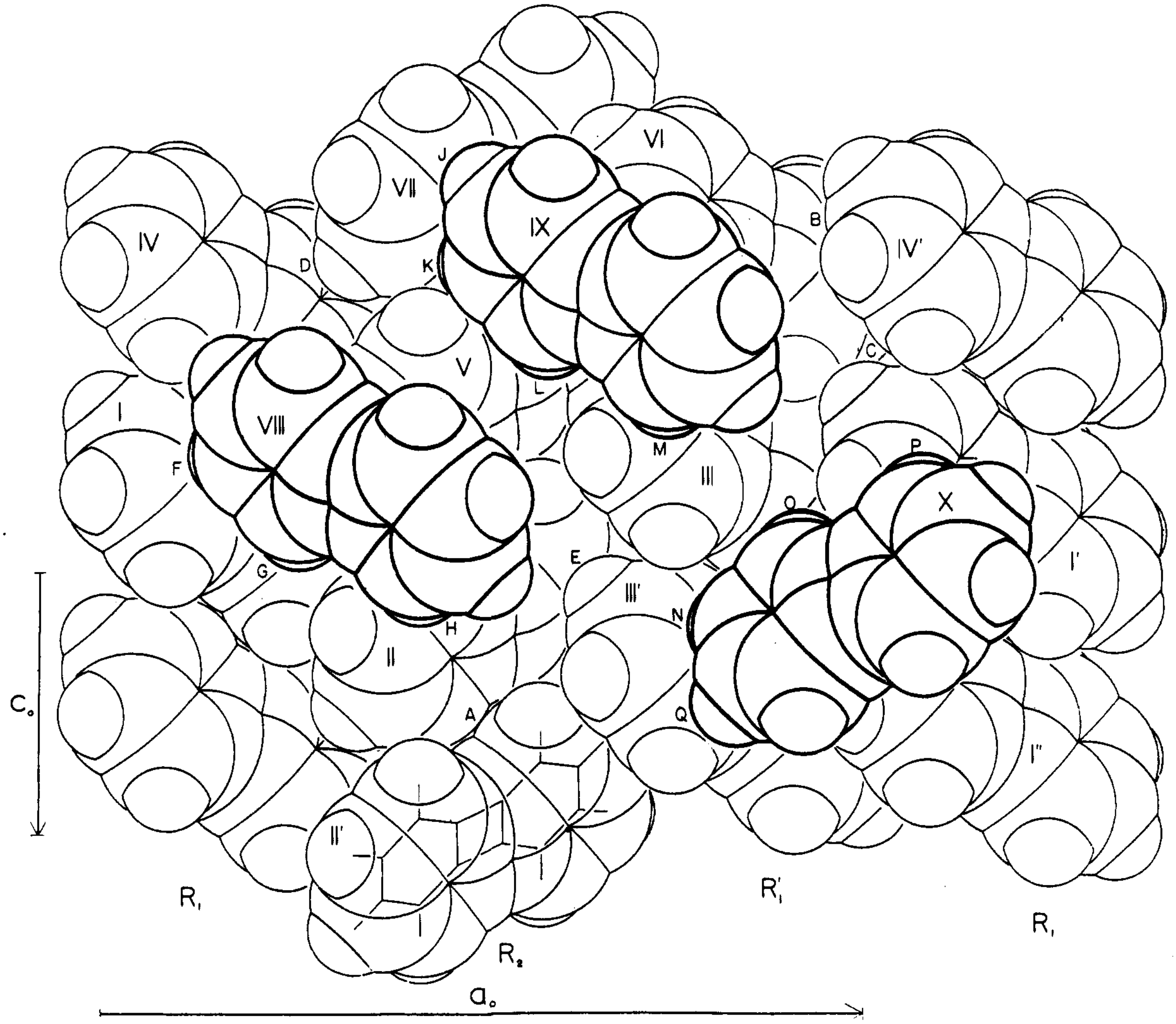

Fig. 6.—Packing drawing of crystal, viewed along *b* axis. Roman numerals correspond to Roman numerals of Fig. 5.

kinds of ribbons are of a different type. A hydrogen atom of VII points toward the center of the six-ring of IV (D). The same kind of contact (not shown) takes place between II′ and III′, while III′ and II interact in an analogous manner at E, and the corresponding interaction between I and II is again not shown in Fig. 6.

The second layer again consists of ribbons of two kinds. Molecules VIII and IX belong to a type $\overline{R}_1$, which is related to ribbons R_1 and R_1' by a glide plane *a*, while X is of a type $\overline{R}_2$ related in a similar manner to the ribbon R_2. It is seen that the ribbons of the type $\overline{R}_2$ in the top layer (represented by molecule X) stretch across the ribbons R_1 and R_1' of the bottom layer and inversely, providing thus a very compact packing. In detail the interactions between the two layers are as follows. A hydrogen atom of molecule VIII points toward the six-ring of molecule I at F, while another hydrogen atom of VIII interacts with molecule I at G. A third hydrogen of VIII interacts with a carbon of II at H, and the hydrogen attached to this carbon of II interacts in an analogous manner (not shown here) with the carbon of VIII that carries the hydrogen first mentioned. Molecule IX lies edge on over the six-ring of VII at J and K. It makes contact with molecule V behind L, a contact of the same nature as the interaction at H, while another hydrogen atom interacts with molecule III at M. A hydrogen atom of molecule X points toward the six-ring of III′ at N in a fashion already encountered at D, E and F. The interactions of X with III and I′ at O and P, respectively, represent the back views of interactions already mentioned. The interaction at O corresponds to interaction H while P corresponds to L. Still another hydrogen atom of X makes contact with III′ at Q.

The two crystallographically different kinds of molecules in the unit cell require discussion of the environment of representatives of each. A molecule with center at 000, as represented by X in Fig. 6, has fourteen neighbors. Four of these belong to the ribbons R_1 and R_1' of the layer below, four to analogous ribbons of the layer above, and six to the same layer (*e. g.*, II, Fig. 6), of which two are in the same ribbon as the molecule considered. A molecule with center at *pqr* as represented by IX in Fig. 6 has fourteen neighbors also. Four of these belong to the layer below, while six belong to the same layer (*e. g.*, III, Fig. 6). Since molecules IX and VIII are related by a space group center the interactions of molecule IX with its four neighbors of the layer above are analogous to the interactions of molecule VIII with the layer below. One of these four interactions, the one between VIII and VI, is weaker than the other three, since this interaction is mainly one between hydrogen atoms.

The following table gives statistics of the intermolecular distances encountered:

Distances between	Molecule with center at 000 and its neighbors	Molecule with center at *pqr* and its neighbors
C...C 3.7–3.8 Å.	6	3
3.6–3.7 Å.	2	8
3.5–3.6 Å.	2	0
C...H 3.0–3.3 Å.	30	31
2.7–3.0 Å.	24	21
2.6–2.7 Å.	2	3
H...H 2.3–2.6 Å.	4	6

The calculated packing distances in general agree with van der Waals distances found for crystals of other aromatic hydrocarbons.[9] Some distances are somewhat short, the two worst kinds being carbon–hydrogen distances of about 2.65 Å. Both these contacts could be improved by bending the C–H bonds in question by a few degrees in the plane of the molecule. A change in the carbon parameters would, of course, change these distances also, so that no real significance can be attached to their shortness.

Of interest is the overlapping of the six-rings of molecules IV′ and VI at B. The distance between the planes of the two molecules is 3.55 Å. which may be compared with the value of 3.66 Å. found for hexamethylbenzene[10]; the interplanar distance in the latter case is partly determined by the size of the methyl groups. The distances involved in the interactions between hydrogen atoms and benzene rings of the type D, E, F and N are quite short. For example the interaction at N involves C . . . H distances of 3.1, 3.0, 2.9, 2.9, 2.9 and 3.0 Å. while the distance between the centers of the six-ring and the hydrogen atom is 2.6 Å. This distance is short enough to show that the van der Waals representation of benzene rings by domes, as suggested by Mack,[11] is inappropriate. A crater-like characterization as used in Fig. 6 represents the actual conditions much better.

The closely knit packing of the biphenylene crystal accounts satisfactorily for the fact that no pronounced cleavages were observed. The packing is different from that characteristic of naphthalene and anthracene.[12]

We wish to express our thanks to Professor L. Pauling for suggesting this problem; to Dr. V. Schomaker for discussion and valuable suggestions; and to him and Mr. J. Donohue for the tracing of the Fourier projections (Figs. 2 and 4). We are indebted to Dr. W. C. Lothrop for the sample of biphenylene.

Summary

The crystal structure of biphenylene is based on a monoclinic unit cell with dimensions a_0 = 19.60 ± 0.03 Å., b_0 = 10.50 ± 0.02 Å., c_0 = 5.84 ± 0.02 Å., $\beta = 91°20' \pm 20'$, containing six molecules. The probable space group is $C_{2h}^5 - P2_1/a$. The centers of two of the six molecules are space group centers. Approximate values of the fifty-four parameters for the carbon atoms are evaluated for planar molecules of dimensions suggested by an electron diffraction investigation.[1] The packing of the molecules is discussed.

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

(11) E. Mack, Jr., THIS JOURNAL, **54**, 2141 (1932); *J. Phys. Chem.*, **41**, 221 (1937).

(12) J. M. Robertson, *Proc. Roy. Soc.* (London), **A140**, 79 (1933). For packing drawings *cf.* R. W. G. Wyckoff, "The Structure of Crystals," Supplement 1930–1934, New York, N. Y., 1935, p. 154–155.