

THE STRUCTURE OF CRYSTALS OF SOME
AROMATIC POLYCYCLIC HYDROCARBONS:
2:13-BENZFLUORANTHENE AND ACENAPHTHENE.

Thesis presented to the University of Edinburgh for
the degree of Ph.D.

by

H. W. W. EHRLICH.

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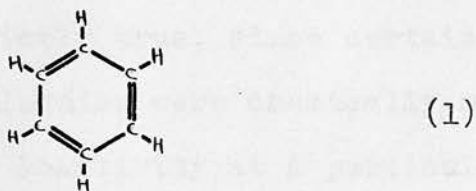
I should like to express my thanks to the University of Edinburgh for an award of a Post-Graduate Studentship to carry out the research described in this thesis. Some of the apparatus was bought with funds supplied by the Agricultural Research Council and the Moray Fund of the University of Edinburgh. However, I feel that this financial support would have availed me little, were it not for the invaluable advice and encouragement that I received from Dr. C.A. Beevers, to whom I wish to acknowledge my indebtedness.

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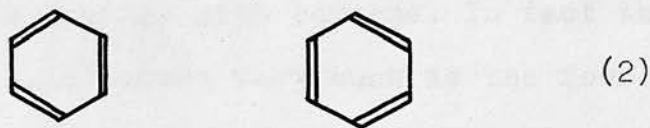
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INTRODUCTION.

In 1865, Kekulé proposed the structure (1) for benzene. This satisfied the condition, that all the six hydrogen atoms in benzene are chemically equivalent. However, this



did not explain why there were only three, and not four, di-substitution products. By making the hypothesis, that the double bonds were oscillating rapidly between the positions shown in (2), this difficulty was overcome. This early work was the



first of a whole host of ring structures for benzene, culminating in the structure we have today.

In our present-day structure for benzene, three of the valency electrons of each carbon atom are involved in something equivalent to a chemical single bond, while the fourth electron of each atom takes part in an electron sheath, above and below the plane of the ring, as in (3). In benzene, these fourth electrons, or π -electrons, are assumed to be completely

delocalised, in the sense that they can move freely about the ring. When this approach was tried



(3)

in other aromatic hydrocarbons, it was found that this could not be strictly true, since certain positions of these molecules were chemically more reactive than others. Reactivity at a particular site in a molecule is associated with excess, or deficiency of electrons, and hence some degree of localisation had to be assumed.

In naphthalene, for example, the 1:2 bond shows more double bond character than is expected from analogy with benzene. In fact the atoms, 1, 2, 3, 4 behave very much as the four atoms in butadiene, for some reactions, e.g. the reduction of naphthalene by sodium in boiling alcohol gives 1:4-dihydronaphthalene. Since in double bonds there is a greater amount of electron density than in an ideal aromatic bond, one comes to the conclusion, that there is a certain degree of localisation of the electrons in the 1:2 bond.

Properties of aromatic bonds, such as length and reactivity, have been the subject of a great deal of research, and the state of the carbon atom in these compounds has been of much theoretical interest. The modern view is that,

although, for rigorous treatment, the molecule must be treated as a whole, very good approximations can be obtained by dealing with the atoms separately. A mathematical approach based on the following premises, has given very promising results.

Three electrons of the carbon atom take part in an sp^2 hybrid orbital, which is represented diagrammatically in (4), the nucleus being at the centre. The three parts of the orbital overlap with atomic orbitals of other atoms to form bonds.



(4)

The fourth electron of each carbon atom remains in its p-orbital, which is perpendicular to the plane of the other one, but when the hybrid orbital has interacted with others, the p-orbital electron takes part in a π -bond with those of the other atoms in the aromatic system.

The geometry of the sp^2 hybrid is very simple. The three main axes of the orbital are coplanar, and at 120° to one another. This agrees very nicely with facts known about the simpler aromatic hydrocarbons, which usually only involve six membered rings. Difficulties arise in molecules which are not planar, or those in which distortions are set up, so as to change the bond

angles from 120° .

Molecules can, however, be constructed so that one of these two distortions must occur, and are consequently of considerable interest. One type is such, that if the molecule remains flat and undistorted, two unbonded parts of the molecule will be forced together, closer than the van der Waals' forces permit.

Examples which have been studied are 3:4-Benzphenanthrene (Herbstein & Schmidt, 1954) and 3:4:5:6-Dibenzphenanthrene (McIntosh, Robertson & Vand, 1952), and the results show that the molecules do deviate from planarity, in order to allow enough room for the atoms. Both these substances show aromatic properties, and the only consoling feature is, that the deviations from planarity at each atom, and of the bond angles, are small.

Another type of molecule in which distortions must occur, is that in which rings, other than six-membered ones are involved. An example is acenaphthene, in which the extra-cyclic bond angles are distorted by the demands of the $\text{CH}_2\text{-CH}_2$ single bond, which can only be of a limited length, and is hardly likely to reach the value of 2.4 \AA , which would be required to avoid any strain. This bond is therefore of very great chemical interest, and measurement of its

dimensions would reveal how much such strains can affect bond lengths. Because of this interest in acenaphthene, there is a correspondingly large amount of work published about it. The first structure determination was carried out by Bannerjee and Sinha in 1937, which was done from magnetic measurements and X-ray diffraction data. The length that they determined for the $\text{CH}_2\text{-CH}_2$ bond was over 2 \AA , as compared with the usual value of 1.54 \AA for a single bond. This was suspicious, to say the least.

Acenaphthene then attracted the attentions of Kitaigorodskii, who condemned the previous work, pointing out errors in intensity measurements, and also the fact that, in their structure, the Indians had molecules within 1.5 \AA of one another. He solved the structure on one projection, and unfortunately succumbed to the temptation of determining the $\text{CH}_2\text{-CH}_2$ bond length by means of eight one-dimensional F's. He published two papers (1947, 1949), in which the bond length dropped to 1.8 \AA , and then to 1.64 \AA . For this last figure, he quoted an accuracy of $\pm 0.04 \text{ \AA}$.

The first substance to be investigated as part of the work for this thesis, was 2:13-Benzfluoranthene. In this molecule even greater strain is put on this bond, and it was

thought that a study of this molecule might give interesting information about the distribution of the stresses. The results, however, showed no extreme lengthening of the bond equivalent to the long bond in acenaphthene. It is expected to be a long aromatic bond, since in none of the Kekulé structures is it ever a double bond. The value, 1.49 Å, that was finally obtained, could easily be expected in an unstrained bond, and this indicated that there was probably no appreciable stress here. Therefore, a more accurate determination of the acenaphthene structure seemed desirable.

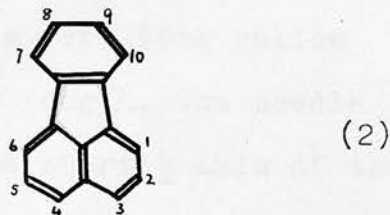
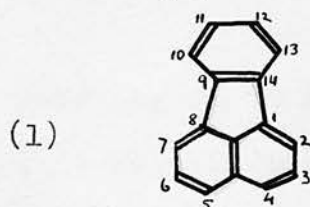
This thesis records the work carried out on the crystal structures of 2:13-Benzfluoranthene and acenaphthene. The structure of the first of these had to be completely determined, whereas in the case of the second structure, only the z parameters had to be determined, the x and y coordinates needing only refinement.

Both these structures were refined to quite high accuracy. In one case low temperature data was used, and in the other Geiger counter measurements at room temperature were employed for one zone of reflections, to increase the reliability of the results.

THE CRYSTAL STRUCTURE OF 2:13-BENZFLUORANTHENE.

NOMENCLATURE.

The carbon atoms in fluoranthene are numbered in two ways. (1) is the method conventionally used in Great Britain, while (2) is more popular in the United States.



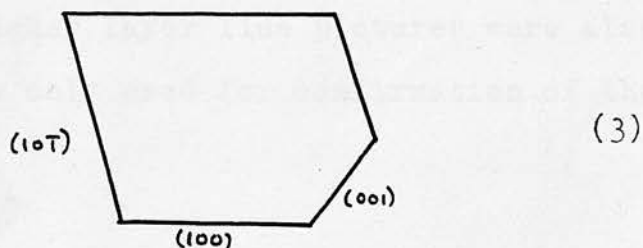
Since the name "fluoranthene" gives no indication of this substance's relationship to naphthalene, it seems illogical to number the atoms as in (1). However, since this work was carried out in Scotland, the British convention was used in naming 2:13-Benzfluoranthene.

EXPERIMENTAL.

Crystal Specimens.

The material was obtained from Dr. O. Kruber of the Gesellschaft fuer Teerverwertung m.b.H., Duisburg-Meiderich, who found them as products of coal tar distillation. No recrystallisation was needed, as the crystals were already of a suitable size.

The crystals were long yellow needles, up to 4 - 5 mm. in length, the needle axis running parallel to the short b axis of the crystal cell. A cross section of a typical crystal perpendicular to the needle axis, is shown in (3). The predominant faces are (100) and $(10\bar{1})$. The (001) face is also frequently observed.



For photography, crystals of approximately circular cross section were used, the diameter of the cylinder being 0.4 mm.

Photography.

A Metropolitan Vickers demountable X-ray tube was used as a source of

X-rays. It was run at 50 kV. and 25 mA., using a copper target and filtering the radiation by means of nickel foils, so as to suppress the Cu K_{β} radiation.

The multiple film technique was used for recording the reflections. In this, an Ilford Industrial G film is placed in front of three Ilford Industrial B films. No paper or foils were placed between the films. The ratios thus obtained between films were $83 : 6\frac{1}{4} : 2\frac{1}{2} : 1$.

The camera used was a normal beam, 10 cm. diameter Weissenberg camera (Beever, 1952). This was used for the room temperature, and was readily converted for the low temperature photography.

The intensity measurements were taken from zero and first layer line Weissenberg photographs. Higher layer line pictures were also taken, but were only used for confirmation of the space group.

Low-temperature apparatus.

Since, in the Beever Weissenberg camera, the film translation is vertical, the cooling apparatus could be set up immediately above the specimen, and supported on the Weissenberg screen. The apparatus itself consists of a Dewar vessel with an overflow tube going through the bottom. This tube has to be coiled

between the two glass vessels, to allow for contraction of the inner one, when liquid air is poured into it. The last part of the delivery tube was of gelatine; this fitted over the crystal specimen so as to direct the cold air past the crystal. Gelatine was used because of its low absorption for X-rays, and because such tubes were easy to prepare by cutting the ends off gelatine capsules designed for holding medicinal preparations.

A glass tube was mounted on the goniometer; the top of the tube was below the X-ray beam. This was necessary to force the cold (and dry) air past the outside of the delivery tube, keeping it free of ice. Ice formed on other parts of the apparatus, and some ice diffraction lines were observed.

The absorption due to ice and gelatine was small, but appreciable. To get the same intensity of low order reflections, which are not noticeably affected by temperature changes, exposures had to be increased by a factor of $1\frac{1}{2}$ for low temperature experiments.

The apparatus, which is shown diagrammatically in figure I, was filled with liquid oxygen, and the flow of cold gas was controlled by a heater. A thermocouple junction was placed just below the crystal, and the

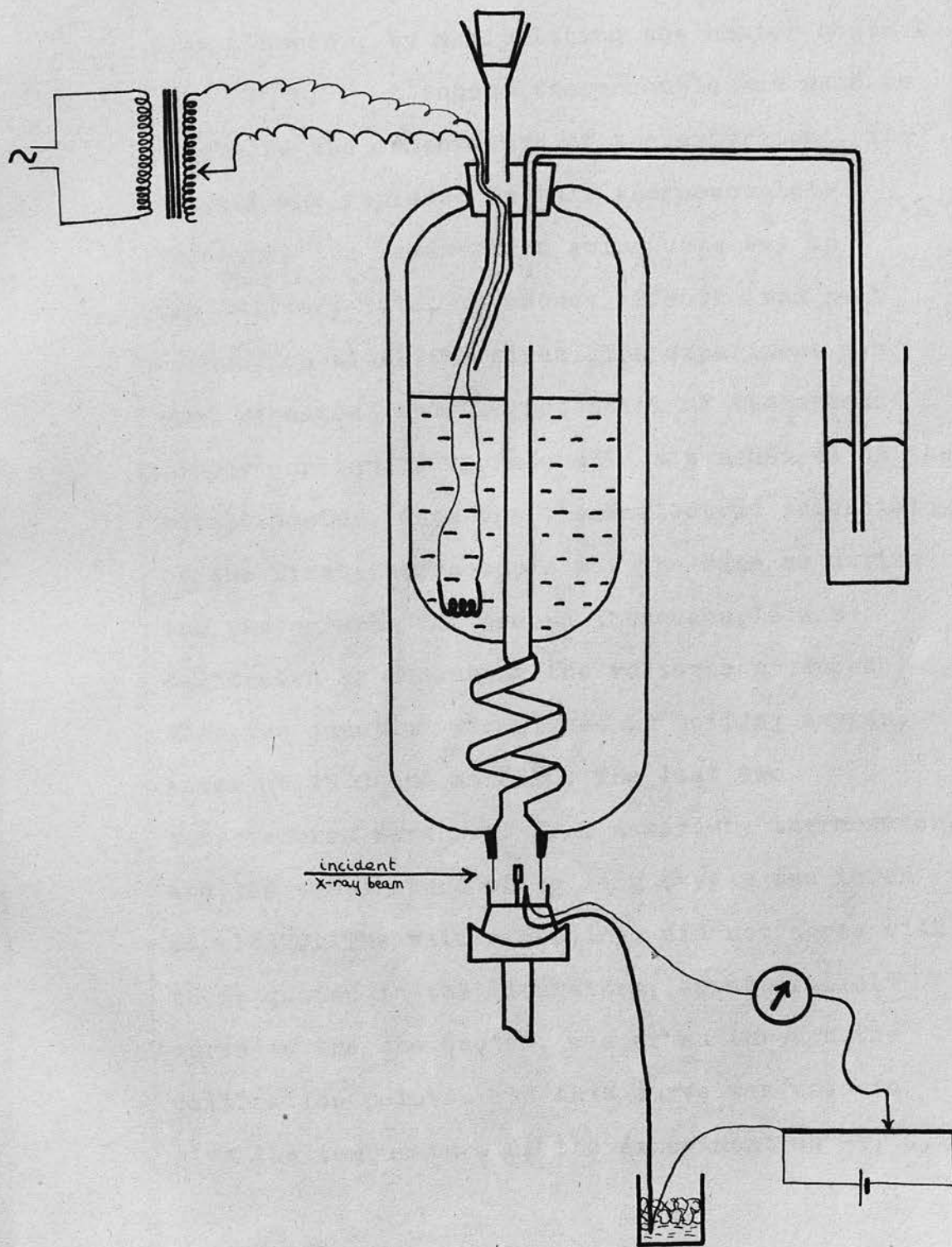


Figure I. Apparatus for cooling the 2:13-Benzfluoranthene crystals.

thermoelectric potential was measured on a potentiometer. The galvanometer reading was kept constant for a predetermined setting of the potentiometer, by manipulating the heater control.

A second thermocouple was used to determine the temperature of the experiment. The crystal was replaced by this thermocouple's junction, the leads first going some way up the delivery tube, to reduce effects from heat conduction along the wires. The experiment was then repeated, and the potential of the second copper-constantan thermocouple was measured on the potentiometer, when the thermoelectric potential of the first thermocouple was the same as during the photograph. The second thermocouple was calibrated by measuring the voltages produced when the junction was placed in boiling oxygen, water at 19°C and at 85°C . The last two temperatures were read from a mercury thermometer, and the temperature of boiling oxygen was taken as -183°C . The values obtained did not agree with those quoted in the literature, so a "parallel" curve to the one quoted, was drawn through the calibration points, and this curve was used to give the temperature of the experiment as -97°C .

Intensity Measurements.

Since the multiple film technique enables one to estimate intensities which differ by as much as a factor of 5000, only one exposure was required for each zone of reflections. This technique is preferable to the multiple exposure procedure, because fluctuations in X-ray output do not affect the ratios between films.

The intensities were estimated by visual comparison against a standard scale. This scale was prepared by taking oscillation photographs of the same crystal that was used for the Weissenberg photograph, using the Weissenberg screen, and exposing for timed intervals. The film is moved along a little after each exposure. The same crystal was used for the two photographs, so that comparisons between spots of the same shape could be done.

This procedure can also be used to get the film ratios for the multiple film technique, by using three films, an Ilford Industrial G film in front of two Ilford Industrial B films.

INTERPRETATION OF THE DIFFRACTION DATA.

Space Group and Cell Dimensions.

The first photographs were taken by rotating the crystal about the needle axis, which proved to be parallel to a very short vector of the crystal lattice. Weissenberg photographs of the zero, first and second layer lines were taken with this setting of the crystal, and two of the three predominant axes of the $h0l$ reciprocal net were chosen.

Oscillation photographs about the same axis, showed that the spots were related to each other by a mirror plane at the zero level. These photographs, then, sufficed to show that the crystal was monoclinic, with the b axis parallel to the crystal needle axis.

Comparison of the zero layer line with upper layer line photographs, revealed that the $h0l$ reflections are systematically absent when h is odd.

Similar photographs were taken with the crystal rotating about its a and c axes. The only systematic absences here, are $h00$ when h is odd, and $0k0$ when k is odd. Fortunately, only one monoclinic space group shows such absences, namely $P2_1/a$ (C_{2h}^5).

The a^* and c^* vectors were

approximately determined from the positions of high order h00 and 00l reflections. The values obtained from these measurements were then used to find the value of β^* by using reflections with h and l so chosen that $ha^* \doteq lc^*$.

This value of β^* was used to obtain more accurate values of a^* and c^* from general h0l's, and the whole process was repeated. These reiterative calculations were continued until no appreciable change occurred in the values of a^* , c^* and β^* . These accurate values of a^* and c^* were also used to get b^* accurately from 0kl's and hk0's.

High accuracy was obtained by using high order reflections, whose θ values can be determined by measuring the distances of spots from shadows cast on the film by knife edges. The positions of the knife edges are constants of the camera, and have been calibrated by quartz powder photographs. Errors due to film shrinkage and absorption were eliminated by using values obtained by extrapolating a plot of a^* , b^* , c^* or $\cos\beta^*$ against $\sin^2\theta$, to $\sin^2\theta = 1$.

At room temperature, the values obtained were $\underline{a} = 19.03 \text{ \AA}$, $\underline{b} = 4.762 \text{ \AA}$, $\underline{c} = 15.81 \text{ \AA}$ and $\beta = 128^\circ 53'$. The values for the crystal at -97°C were slightly, but significantly different. This effect is due to

thermal contraction.

The density of the crystals was determined by flotation, and is 1.345 g/cc. This means that there must be four molecules in every unit cell.

Determination of the Trial Structure.

The cell dimensions showed that the first projection to tackle was on to (010), since good resolution of the atoms could be expected, as the b axis is so short.

At this stage of the investigation, there was doubt as to whether the molecule was planar or not. Now the space group $P2_1/a$ is a very common space group for flat molecules, and the larger of these also show a b axis of length 4.7 Å. It thus seemed reasonable to assume, that the structure of 2:13-Benz-fluoranthene would not be unlike that of phthalocyanine (Robertson, 1935), coronene (Robertson & White, 1945) or ovalene (Donaldson & Robertson, 1953), and hence a planar model was favoured.

The structure was determined by solving the Patterson projection down the b axis. Since the intensities of the reflections fall off very rapidly with increasing $\sin\theta$, it was decided to boost the high order reflections by

multiplying the F^2 's by a term, $\exp(4.6\sin^2\theta)$, thus sharpening the Patterson function.

The Patterson function will contain vectors of two types, the inter- and the intra-molecular vectors. In molecules with benzene rings, which are related to others by a centre of symmetry, some of these vectors will coincide to give very heavy peaks in a vector map. For example, when a naphthalene nucleus is related to another one by a centre of symmetry, two vectors occur six times, and one vector occurs ten times. The vectors are shown in figure II, and it is clear that these peaks will be collinear. Now 2:13-Benzfluoranthene has three naphthalene nuclei, AB, BC, & CD (see figure III). Also, rings A & C, B & D and A & D are nearly parallel, giving rise to two sharp and one diffuse peak for each pair of rings.

The intra-molecular vectors are no less interesting. Firstly, one will expect the benzene ring vectors. There are two strong sets of these, corresponding to vectors along the edges, and the short diagonals of the hexagon. In molecules with several benzene rings, such as this one, the long diagonal vector of the hexagon should also be observed. Inter-benzene ring multiple vectors will also arise, and three of these will coincide with the short diagonal vectors of the

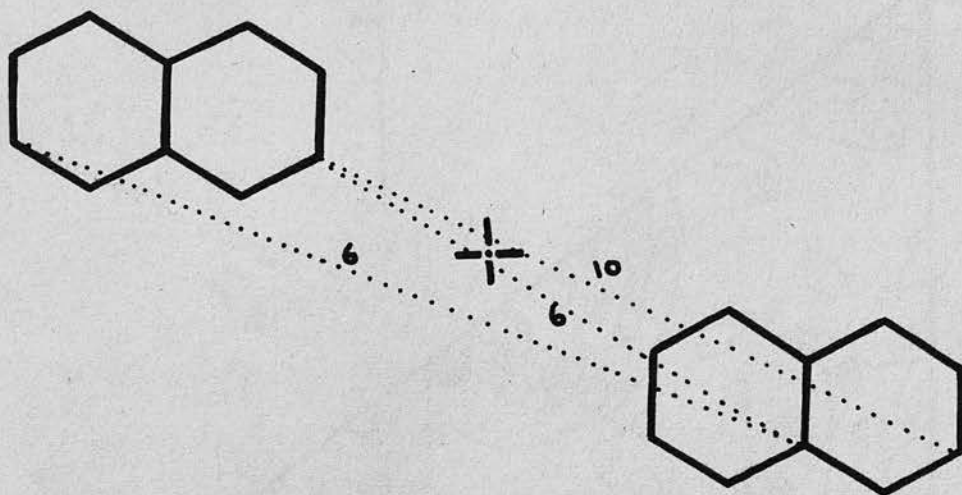


Figure II. Intermolecular multiple vectors.

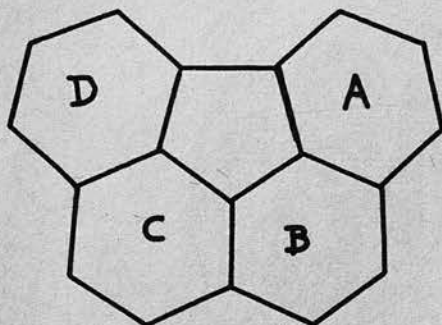


Figure III. The 2:13-Benzfluoranthene Molecule.

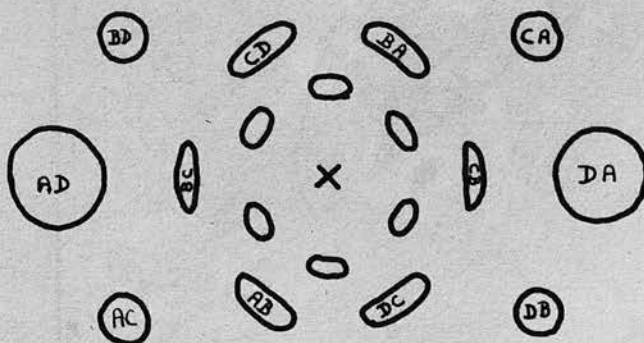


Figure IV. The intramolecular vectors of
2:13-Benzfluoranthene.

benzene ring. These intra-molecular vectors are shown in figure IV.

The Patterson projection calculated from the intensities is shown in figure V, and considering only the detail around the origin, the orientation of the molecule is immediately determined, by comparing the peaks with the vectors in figure IV.

Also, the inter-molecular vectors between rings B & C and A & D will lie on parallel lines. In the map there are lines of peaks in the expected direction, which puts the trial molecular structure almost beyond doubt.

Superpositions were carried out with this trial molecule. Two Patterson maps, differing in relative position by an intra-molecular vector from one atom, were superposed. All low ground in either map was traced on to a third piece of paper. This was repeated with another vector from the same atom, and the low ground traced on to the same piece of paper, as before. This was done for all the vectors from this one atom. The resulting picture left only a little common high ground, these sites being possible positions for other atoms. By selecting sites, so that a molecule symmetrically disposed to the original molecule could be discerned, the position of the second molecule was found. The

centre of symmetry was placed half-way between the molecules, and hence atomic coordinates could be deduced.

As a final check, the positions of all the multiple vectors already mentioned, were plotted for the trial crystal structure, and compared with the Patterson map.

With these approximate atomic positions, some of the strong high order reflections were given signs, by using graphical methods, and these waves were then used to obtain more accurate coordinates for the atoms, as was done for coronene and ovalene. The reflections used were $14,0,\overline{13}$, $14,0,\overline{10}$, $14,0,3$, $0,0,14$ and $2,0,\overline{14}$.

This projection was then refined to some accuracy by means of difference maps, before proceeding to the determination of the y coordinates of the atoms.

These were again determined by using a Patterson synthesis. From the b axis projection, it is not clear whether, in the c axis projection, the molecule lies about a centre of symmetry or a twofold screw axis. The Patterson projection showed very low ground at $0,\frac{1}{2}$, which immediately eliminated the second possibility. Use was again made of the superposition method, to find the position of the centre of symmetry, relative to the molecule.

Refinement of the Structure.

The structure was refined solely by difference syntheses. After six stages of refinement on the (010) projection, regions of positive electron density were observed at sites, where hydrogen atoms might be expected. Structure factors from the next stage onwards, included contributions from hydrogen atoms. In all, nine cycles of refinement were carried out on the h0l's.

The a and c axis projections were more troublesome to refine, because of bad resolution of the atoms. Four and fourteen cycles of refinement were required for these two projections respectively.

Although, at this stage, the agreement between calculated and observed structure factors was quite good, the difference maps were most unpromising. The (010) projection, which was the best, showed that some of the atoms lay in negative ground on the map, which was, in places, as low as $-0.6 \text{ e}/\text{\AA}^2$. The other projections were very unpleasant too, with unexplainable peaks up to $1.5 \text{ e}/\text{\AA}^2$ in magnitude.

It was thought that these effects might be due to poor intensity estimation, combined with effects from the large value of B, the Debye factor (4.31\AA^2). Since crystals with large temperature factors have small high order reflections, with many unobserved ones among them,

difference terms from these might be quite badly in error. The obvious way of overcoming this difficulty was to use results from photographs taken of a cooled crystal.

A comparison of the low temperature photograph with that taken at room temperature, showed that no radical change in the structure had taken place. The resulting difference map, showed exactly the same disturbing features. This time the effect was even more marked, and since this was obtained from a new set of data from a different crystal, the effect must be real. The only satisfactory explanation is, that all the atoms in the molecule do not vibrate to the same extent.

Temperature factors were then estimated for each atom, and the refinement proceeded, adjusting the values of x, z and B for each atom at every stage. The work was made less tedious by employing a new method for dealing with the temperature factors. Only four more cycles of refinement were required for this projection. The remaining electron density detail that could be considered significant, could be explained by assuming that some of the atoms vibrate anisotropically. As the computation involved to correct for this, would have been prohibitive, it was decided not to continue beyond this stage. The reliability index, $R = 100(\sum |F_o - F_c|) \div \sum |F_o|$,

for this projection was 14.9, treating the unobserved reflections as having $|F_o| = 0$. When the unobserved reflections were given a value of $\frac{\sqrt{2}}{2}$ (minimum observed), the value of R dropped to 11.8. In both these calculations of the reliability index, the contributions from four reflections (200, 002, 20 $\bar{2}$, 20 $\bar{4}$) were omitted, as the large differences recorded were thought to be due to extinction effects.

The other two projections again proved to be more difficult to refine, and 10 cycles of refinement were carried out on the a axis projection, and 6 cycles on the c axis projection. The resulting difference maps again are rather disappointing, some peaks of electron density being as high as 0.6 e/ \AA^2 . However, since the resolution on these projections is abominable, one ought not to be too critical. Under the circumstances, it is doubtful whether ordinary Fourier syntheses could have been successfully used to refine the structure. In support of this contention, a Fourier projection down the a axis is shown in figure VI. The corresponding map for the b axis projection is also shown, on a different scale, for comparison. The R-factors for these projections were 17.1 and 19.8 for the a and c axes respectively. If the unobserved reflections are corrected for, as previously, these values

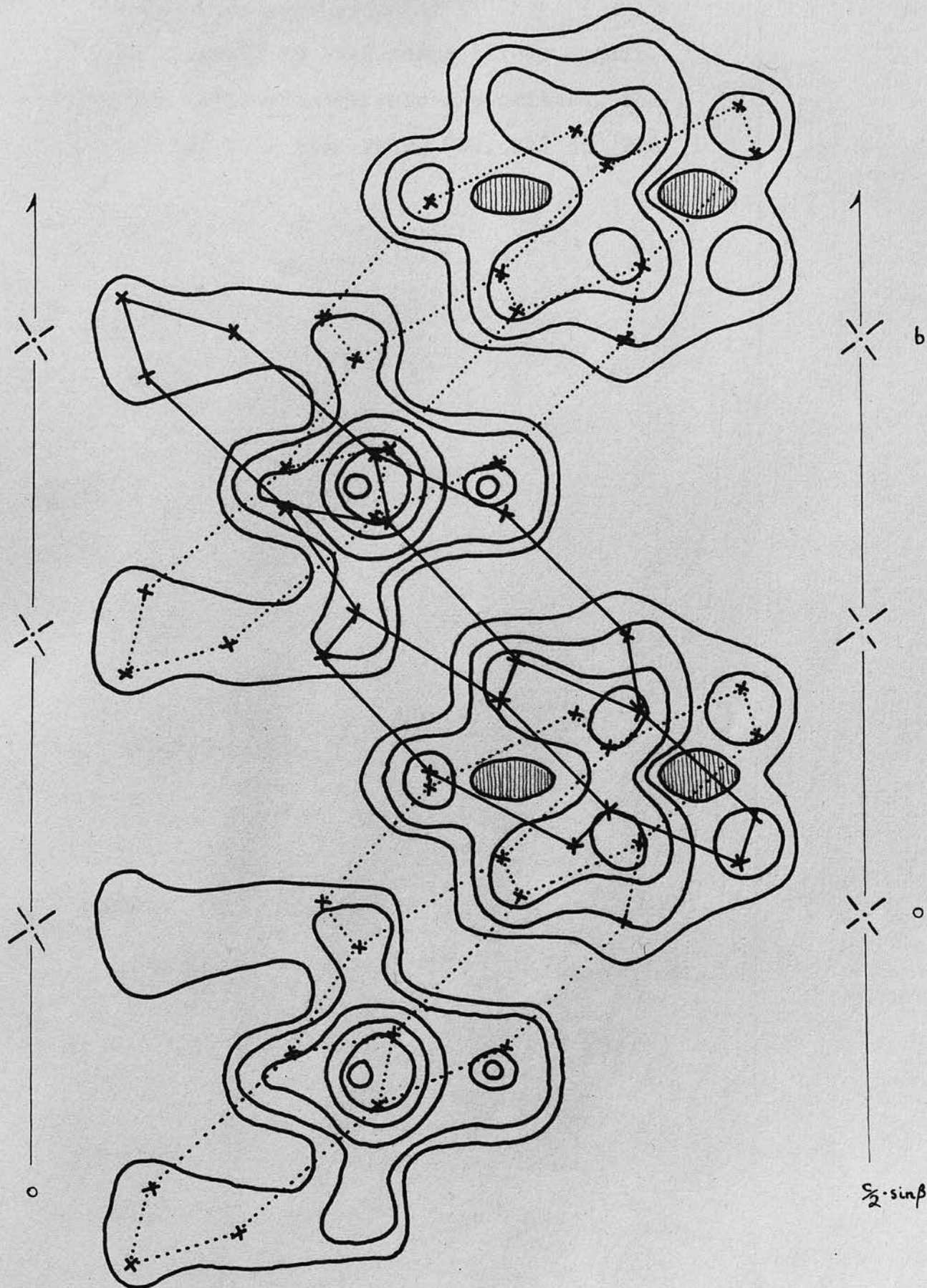


Figure VI. The a axis electron density projection of
2:13-Benzfluoranthene.

Contours every 3 e. \AA^{-2} , first contour at 9 e. \AA^{-2} .

reduce to 13.9 and 13.2 respectively. Again possible extinction effects are omitted, the reflections this time being 002, 012 and 200.

h	k	l	d (Å)	Accuracy
13	9	0	13.9	± 0.03
13	0	0	13.2	± 0.03
0	0	200	11.5	± 0.03
0	12	0	11.5	± 0.03
0	0	200	11.5	± 0.03

The procedure for determining the d-spacing values was calculated by Hurler & Jørgen (1954).

The hydrogen 1-curve used was taken from the International Tables.

The average bond positions were chosen as the first approximation, but their positions were not refined. The difference between the calculated and observed intensities was not refined. The difference between the calculated and observed intensities was not refined. The difference between the calculated and observed intensities was not refined.

DETAILS OF THE ANALYSIS.

Cell Dimensions and Space Group.

	At -97°C.	At +23°C.	Accuracy.
a (Å)	18.83	19.03	± 0.03
b (Å)	4.733	4.762	± 0.005
c (Å)	15.69	15.81	± 0.03
β	129° 3'	128° 53'	± 3'
Cell volume (Å ³)	1086	1115	± 4
Density calc. (g/cc)	1.384	1.348	± 0.005
Density obs. (g/cc)	-	1.345	± 0.013

Monoclinic Space Group $P2_1/a$ (C_{2h}^5), $Z = 4$.

Atomic Coordinates.

The f-curve for carbon that was used, was that calculated by Hoerni & Ibers (1954).

The hydrogen f-curve used was taken from the International Tables.

The hydrogen atom positions were chosen on theoretical grounds, and their sites were not obtained from a difference map; hence they are of no value for the determination of C-H bond lengths.

The number of a hydrogen atom is the same as that of the carbon atom to which it is attached.

Parameters of the Carbon Atoms.

Atom	x	y	z	B(\AA^2)
1	0.931	0.428	0.058	3.00
2	0.858	0.563	0.047	2.85
3	0.834	0.504	0.113	3.00
4	0.886	0.313	0.200	2.37
5	0.875	0.206	0.277	3.15
6	0.930	0.003	0.355	2.85
7	0.005	0.875	0.362	2.85
8	0.073	0.662	0.435	3.00
9	0.138	0.576	0.427	3.15
10	0.140	0.692	0.343	3.00
11	0.201	0.624	0.320	3.75
12	0.189	0.756	0.232	3.50
13	0.121	0.970	0.167	3.25
14	0.063	0.041	0.187	2.85
15	0.983	0.228	0.143	3.00
16	0.955	0.192	0.207	2.37
17	0.012	0.970	0.287	2.37
18	0.076	0.888	0.276	2.85

Parameters of the Hydrogen Atoms.

Atom	120x	120y	120z
1	114	56	1
2	21	36	1
3	93	72	12
5	99	36	33
6	110	112	49
8	9	70	59
9	22	52	58
11	30	56	44
12	28	86	27
13	14	10	12

Structure factors.

The calculated and observed values for the structure factors are shown in the table below. This reduced form was readily available, and is used here to save space.

hko reflections

h	k	o	F _o	F _c	h	k	o	F _o	F _c	h	k	o	F _o	F _c	h	k	o	F _o	F _c	
12	5.1	6.4	3	-6.2	3.4	15	1.7	3.4	8	-9.1	9.9	1	4.0	4.5	13	3.3	<2.5	9	-1.1	<2.5
13	0.7	<4.0	4	-9.1	10.2	16	1.5	<3.0	9	6.3	3.4	2	1.1	<3.9	14	-4.6	4.5	10	4.1	4.1
14	-7.1	7.2	5	2.9	<2.9	17	-1.2	<2.4	10	-6.4	6.8	3	-1.6	<3.9						
15	4.4	<3.7	6	-8.4	10.4				11	0.4	<3.9	4	-2.7	3.5						
16	6.8	7.1	7	5.4	5.5	k=3			12	-2.6	<3.8	5	-12.5	13.1	k=5	6.6	6.3	k=6	3.3	<2.0
17	8.6	7.1	8	-7.3	7.0	h=1	10.0	9.6	13	0.4	<3.5	6	7.3	5.5	2	-2.7	<3.6	1	1.7	<2.0
18	7.6	6.2	9	12.2	11.6	2	-4.8	<3.2	14	3.2	<3.2	7	-8.9	9.0	3	4.2	<3.6	2	2.5	<1.8
			10	-9.5	10.1	3	-5.1	4.5	15	7.6	9.2	8	1.1	<3.9	4	-2.9	<3.5	3	-1.9	<1.6
			11	4.9	6.0	4	8.9	11.5	16	4.7	3.0	9	2.0	<3.7	5	1.6	<3.4			
			12	12.5	11.5	5	-1.3	14.0				10	-2.8	<3.6	6	-0.3	<3.2			
			13	8.3	8.9	6	2.2	<3.7	k=4			11	3.1	<3.3	7	-2.6	<3.0			
			14	11.7	9.7	7	-10.7	11.2	h=0	10.7	11.2	12	-1.0	<3.0	8	2.1	<2.8			

hkl reflections

h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	
8	4.7	6.2	9	1.5	<2.8	h=14	21.8	20.8	-10	0.4	<3.4	-7	-5.1	3.1						
9	-6.3	6.2	10	2.7	<2.9	1	-8.0	6.7	-11	22.3	19.5	-8	7.7	5.8						
10	2.0	<2.0	-11	-12.6	12.3	2	-11.9	10.9	-12	-11.5	8.2	-10	-7.0	6.0						
-1	-15.9	16.6	-12	-1.2	<3.2	3	28.3	26.8	-13	3.9	4.4	-11	-1.8	<3.1						
-2	-39.0	42.2	-13	28.3	26.8	4	-8.8	8.7	-14	2.4	<3.3	-12	0.3	<3.1						
-3	5.8	5.1	-14	6.5	5.3	5	-5.2	6.2	-15	5.6	4.9	-13	5.5	5.3						
-4	-20.9	20.7	-15	-5.2	6.2	-1	-11.9	10.9	-16	7.7	6.9	-14	-2.0	<3.0						
-5	-11.0	10.2	-16	-18.2	16.0	-2	12.0	12.3	-17	5.8	7.1	-15	-3.5	3.6						
-6	33.1	32.8	-17	-4.2	4.4	-3	12.0	12.3	-18	-2.8	<3.6	-16	0.6	<2.4						
-7	25.7	24.3	-18	4.5	4.0	-4	0.4	<3.3	-19	-3.5	3.4	-17	-4.3	<2.4						
-8	-4.4	<2.5	-19	-1.2	<1.9	-5	12.6	11.7	-20	5.4	6.4	-18	-7.4	11.4						
-9	-29.0	27.2				-6	5.4	6.4				-19	1.9	<1.5						
			8	4.7	6.2	h=12			-7	0.0	<3.2	-10	-1.4	<2.1						
			9	-6.3	6.2	1	-2.7	<3.4	-8	-9.9	8.0	1	-0.2	<1.4	h=22					
			10	2.0	<2.0	2	8.4	8.7	-9	-18.4	14.8	-2	9.9	8.2	1	1.3				
			-1	-15.9	16.6	3	7.2	6.9	-10	-46.2	42.9	-3	-3.5	<2.8	-4	-3.0	2.5			
			-2	-39.0	42.2	4	-21.8	21.2	-11	-14.7	15.1	-7	-7.5	6.0	5	-6.5	6.0			
			-3	5.8	5.1	5	-12.3	11.3	-12	14.0	13.8	-8	-2.1	<2.3	6	-2.1	<2.3			
			-4	-20.9	20.7	6	-9.3	7.3	-13	-37.7	35.5	-9	10.9	9.8	-9	2.0	<2.4			
			-5	-11.0	10.2	7	3.7	2.7	-14	4.9	4.9	-6	6.3	6.4	-10	-1.7	<2.5			
			-6	33.1	32.8	8	-5.2	4.4	-15	5.8	7.1	-7	-5.7	4.9	-11	1.9	<2.6			
			-7	25.7	24.3	9	12.2	12.9	-16	8.3	8.2	-8	6.0	3.8	-12	5.7	7.2			
			-8	-4.4	<2.5	10	10.6	11.5	-17	4.3	<3.1	-9	-10.0	8.1	-13	-0.5	<2.4			
			-9	-29.0	27.2	11	22.0	23.6	-18	1.1	<2.7	-10	14.2	12.3	-14	0.3	<2.4			
			h=0	-4.5	5.0	12	-5.4	3.1	-19	-2.3	<2.3	-11	21.0	18.7	-15	-2.0	<2.3			
			1	-0.9	<3.2	13	3.9	<2.9	-20	-0.4	<3.5	-12	0.3	<3.4	-16	-10.2	11.4			
			2	-5.9	6.2	14	3.9	<2.9	-13	-1.8	<3.4	-17	0.9	<1.8	-18	0.9	<1.8			
			3	-14.8	14.4	15	20.9	20.9	-14	2.9	4.6	-18	6.3	4.7						
			4	-10.4	10.7	16	11.3	9.2	-15	19.5	18.8	-14	2.9	4.6						
			5	5.2	4.4	17	-17.4	16.0	-16	1	-35.9	18.6	-15	3.0	<3.2					
			6	1.2	<3.1	18	15.0	12.0	-17	2	0.6	<2.3	-17	-2.1	<3.0					
			7	4.3	4.0	19	-22.0	25.0	-18	3	6.7	4.9	-18	-0.7	<2.8					
			8	8.7	9.0	20	-27.4	25.0	-19	4	6.7	4.9	-19	-6.1	4.6	h=11	6.5	5.6		
			9	-4.5	2.2	21	-7.4	4.4	-20	5	12.6	11.8	-19	7.1	9.4	-12	-5.9	6.0		
			10	-17.4	18.0	22	14.9	16.0	-21	6	-22.0	23.7	-20	2.2	<3.0	-13	-4.1	3.4		
			11	7.6	8.4	23	-12.6	8.6	-22	7	-3.1	<3.4	h=20	0.0	<1.7	-14	4.4	1.8		
			12	17.2	20.9	24	14.9	16.0	-23	8	11.4	12.3	-15	1.4	<2.1	-15	4.4	1.8		
			13	3.6	<3.1	25	-12.6	8.6	-24	9	-3.1	<3.4	h=22	0.0	<1.7	-16	4.4	1.8		
			14	29.6	28.2	26	17.0	9.2	-25	10	11.4	12.3	-16	-1.3	<2.1	-17	4.4	1.8		
			15	-47.2	45.2	27	1.0	<3.0	-26	11	-6.3	5.6	-17	-1.3	<2.1	-18	4.4	1.8		
			16	15.5	12.3	28	4.0	<2.7	-27	12	-6.5	4.9	-18	1.4	<2.4	-19	4.4	1.8		
			17	11.3	12.1	29	-2.7	2.2	-28	13	-18.2	15.4	-19	5.9	3.4	-20	4.4	1.8		
			18	2.2	<2.7	30	6.4	4.9	-29	14	-30.1	27.9	-20	5.2	5.1	-21	4.4	1.8		

0kl reflections

h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	
13	-5.7	5.1	7	2.6	<4.4	2	-10.1	12.3	12	-1.4	<1.4	8	1.8	<2.4						
14	-5.4	5.7	8	15.8	17.0	3	-12.0	14.5	13	4	-2.7	<4.5	9	-1.6	<1.4					
			9	-0.7	<4.4	4	0.6	<4.7	14	5	0.6	<4.7								
			10	-1.3	<4.2	5	0.6	<4.7	15	6	0.1	<4.3								
			11	5.3	4.4	6	0.1	<4.3	16	7	0.1	<4.3								
			12	1.7	<3.9	13	5.9	7.0	17	8	5.9	7.0								
			13	1.9	<3.9	14	0.0	<3.8	18	9	0.0	<3.8								
			14	1.1	<4.3	15	0.7	<3.3	19	10	0.7	<3.3								
			15	-14.8	14.1	16	12.3	13.4	20	11	0.0	<2.7								

To be certain that the structure was correct, some general $F(hkl)$'s were calculated. As this was only a check, hydrogen atom contributions were not included, nor were the temperature factors for the carbon atoms very accurate. These reflections were recorded at room temperature on a first layer line Weissenberg photograph, the crystal rotating about the b axis. For these reflections, therefore, $k=1$.

F_c	F_o	F_c	F_o	F_c	F_o
$h=0$		$h=2$		$h=4$	
$l=2$	-82 95	$l=6$	-11 8	$l=4$	7 7
3	22 24	-1	11 20	-1	6 7
4	24 21	-2	-12 16	-2	26 39
5	5 0	-3	-18 20	-3	15 12
6	-6 5	-4	2 6	-4	-11 10
$h=1$		-5	1 0	$h=5$	
$l=1$	-32 41	-6	4 0	$l=0$	1 5
2	141 145	$h=3$		1	-8 7
3	0 0	$l=0$	83 96	2	27 26
4	-2 5	1	-32 38	3	16 16
5	-3 0	2	-48 47	-1	-6 9
6	15 15	3	33 31	-2	1 0
-2	-9 15	4	-18 21	-3	8 10
-3	6 7	5	-10 10	$h=6$	
-4	1 3	-1	22 26	$l=0$	8 8
-5	9 11	-2	44 51	1	21 18
-6	26 25	-3	10 9	2	-3 5
$h=2$		-4	-4 0	-1	-4 0
$l=0$	109 121	-5	-2 4	-2	9 10
1	-56 56	$h=4$		$h=7$	
2	-82 70	$l=0$	19 22	$l=0$	-11 9
3	-10 13	1	10 14	1	-1 0
4	18 17	2	1 9	-1	-4 3
5	8 7	3	-30 28		

Molecular Dimensions.

The atomic coordinates were referred to orthogonal axes, and the mean plane through them was determined by the method of least squares. The plane thus determined, was then referred to the crystallographic axes, and is

$$8.7599x + 5.433y + 7.7587z = 2.191,$$

where x, y and z are the fractional coordinates referred to the crystal cell axes a, b and c.

The displacement of each atom from this plane is as follows :-

Atom	Displacement (Å)	Atom	Displacement (Å)
1	-0.013	10	0.014
2	-0.008	11	0.007
3	-0.019	12	-0.039
4	0.039	13	0.001
5	-0.011	14	0.021
6	-0.021	15	0.025
7	-0.011	16	0.041
8	-0.008	17	-0.020
9	0.017	18	0.004

The mean plane of the molecule is inclined at 44.2° to the (010) face, the maximum slope being nearly parallel to the $(10\bar{1})$ plane.

The bond lengths are best shown in a diagram. Figure VII shows the bond lengths as determined individually, and as a weighted mean of

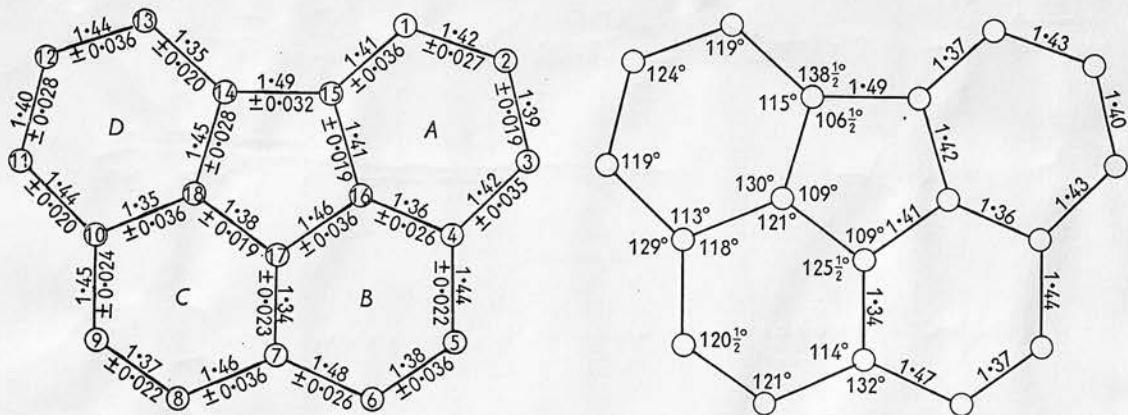


Fig.VII (a) The bond lengths and their standard deviations. (b) Mean bond lengths and angles.

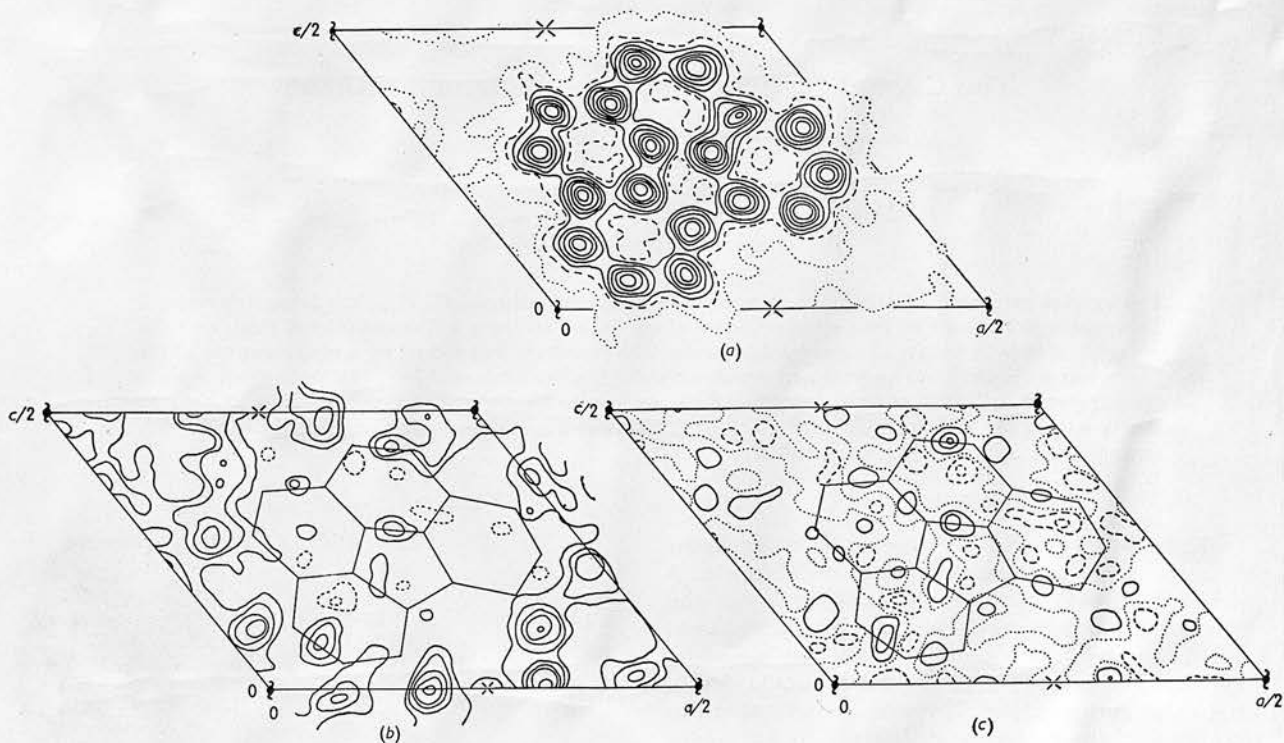


Fig.VIII (a) Electron-density projection on (010). The contours are at intervals of 1 e.Å^{-2} . The one-electron contour is dotted, and the two-electron contour is shown by a broken line. (b) A difference synthesis on (010) with only the carbon atoms subtracted. Contours are drawn every 0.2 e.Å^{-2} , the zero contour being omitted and the negative contours broken. (c) The final $F_o - F_c$ synthesis of the $(h0l)$ reflexions, with contours every 0.2 e.Å^{-2} , the zero contour being dotted and the negative contours broken.

the values of two chemically equivalent bonds. The mean angles are also shown.

Estimation of Accuracy.

The standard deviations of the electron density and of the atomic coordinates were calculated by the method of Cruickshank (1949). For these calculations, the differences due to possible extinction effects, were omitted.

The standard deviations of the atomic coordinates are

$$\sigma(x) = \sigma(z) = 0.012 \text{ \AA}$$

$$\sigma(y) = 0.025 \text{ \AA}.$$

The standard deviations of the electron density are

$$\sigma(\rho) = 0.18 \text{ e/\AA}^2 \text{ for the 010 projection,}$$

$$\sigma(\rho) = 0.41 \text{ e/\AA}^2 \text{ for the 100 projection, and}$$

$$\sigma(\rho) = 0.37 \text{ e/\AA}^2 \text{ for the 001 projection.}$$

Hence one can calculate the standard deviations of the bond lengths. These are shown along the appropriate bond in figure VII. For the mean bond lengths, the standard deviation is 0.02 \AA , except for the bond $C_{14}-C_{15}$, for which the standard deviation is 0.03 \AA .

Difference maps.

The final difference syntheses are shown in figures VIII, IX and X. A map showing the

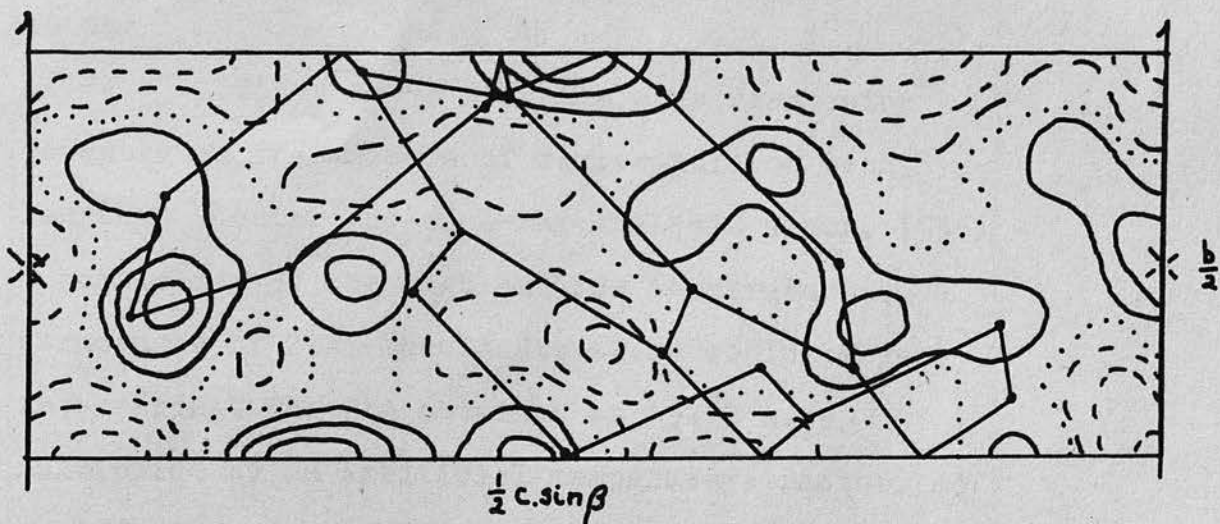


Figure IX. The $(F_0 - F_c)$ synthesis for the $F(0kl)$'s.
Contours as in figure VIII (c).



Figure X. The $(F_0 - F_c)$ synthesis for the $F(hk0)$'s.
Contours as in figure VIII (c).

hydrogen atoms in the b axis projection is also shown.

Since there has been some discussion recently on the effects of temperature on bond lengths, (Conference of X-ray Analysis Group, 1956) a comparison of the high and low temperature structures of 2:13-Benzfluoranthene would be very interesting. The F's obtained at -97°C were multiplied by an artificial temperature factor, so as to bring them on to the same scale as the room temperature data. An $(F_{\text{cold}} - F_{\text{hot}})$ synthesis was then calculated, and the result is shown in figure XI.

There are some changes in the relative values of B for the atoms, but more remarkable are the peaks near the atomic sites. These resemble "shifts" of the atoms, the molecule apparently swelling at low temperatures. Since the cell edges contract at these temperatures, it seems very likely that the molecule does not alter its dimensions. The effect of temperature on bond length is small compared with that on the van der Waals radii. It is the latter effect that is observed as thermal expansion in 2:13-Benzfluoranthene.

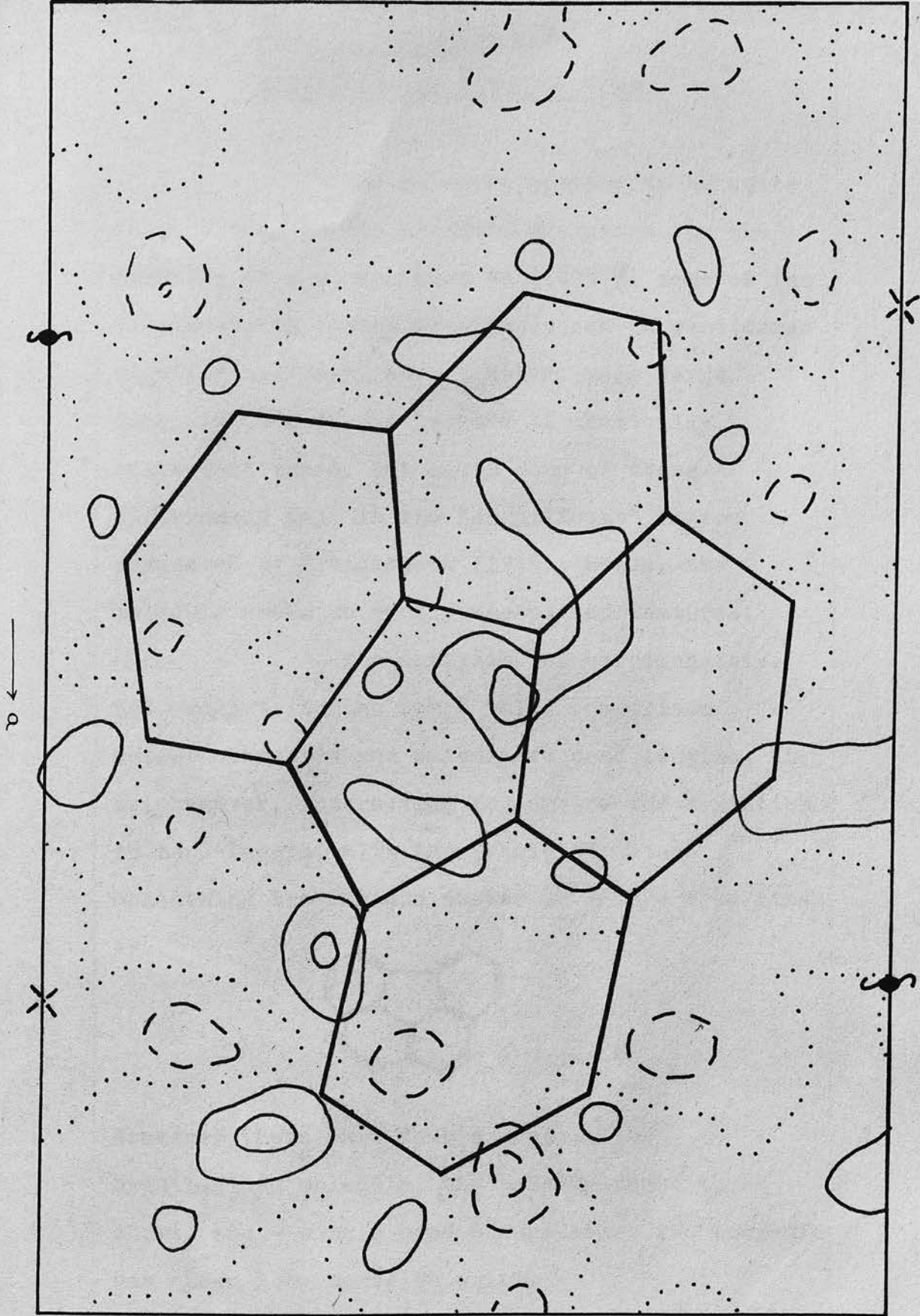


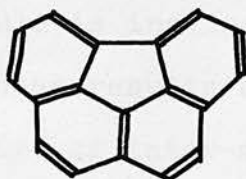
Figure XI. The $(F_{\text{cold}} - F_{\text{hot}})$ synthesis
for 2:13-Benzfluoranthene.

Contours as in figure VIII (c).

DISCUSSION OF THE STRUCTURE.

The molecule appears to be quite flat, since, as the standard deviation for the position of a carbon atom is 0.028 Å, none of the displacements listed previously can be considered significant. There are, however, some large discrepancies in the lengths of chemically equivalent bonds, but again none of these differences fall in the "significant" region suggested by Cruickshank (1949). Hence, the molecule shows no really unexpected features.

The analysis is, unfortunately, not accurate enough for a valid comparison between observed and calculated bond lengths. It is, however, interesting to compare the variation in bond length, with the Kekulé structure containing the maximum number of Kekulé type rings



Wherever there is a double bond in the hypothetical molecule, the bond is found to be short, and a single bond occurs where the analysis has shown long bonds to exist.

Probably the most interesting bond in the molecule is $C_{14}-C_{15}$, and it is a pity

that its length is so dependent on the most inaccurate coordinate, the y coordinate. It is nevertheless safe to say, that the bond is significantly longer than a normal benzene ring bond of 1.39 Å, but not longer than a single bond. This therefore casts doubt on the validity of Kitaigorodskii's claim, that his bond length in acenaphthene is accurate to within ± 0.04 Å. The stress appears in the bond angles, some of which are very different from the ideal 120° , and it seems that bond lengths remain within fixed limits, no matter what the strain.

The features of crystallographic interest are the van der Waals distances. All contacts between molecules less than 4.10 Å are shown in figure XII. The thickness of the aromatic molecule is given as

$$b \cdot \sin 45.8^\circ = 3.40 \text{ \AA},$$

since the molecule is inclined at 45.8° to the b axis. None of these results conflicts with our previous knowledge of inter-molecular approach distances.

The structure is very similar to that of phthalocyanine, coronene and ovalene. In these the molecules make angles of 45.8° , 46.3° and 47.1° respectively, with the b axis. These are centrosymmetric molecules, and the unique portion of the crystal cell contains half a molecule.

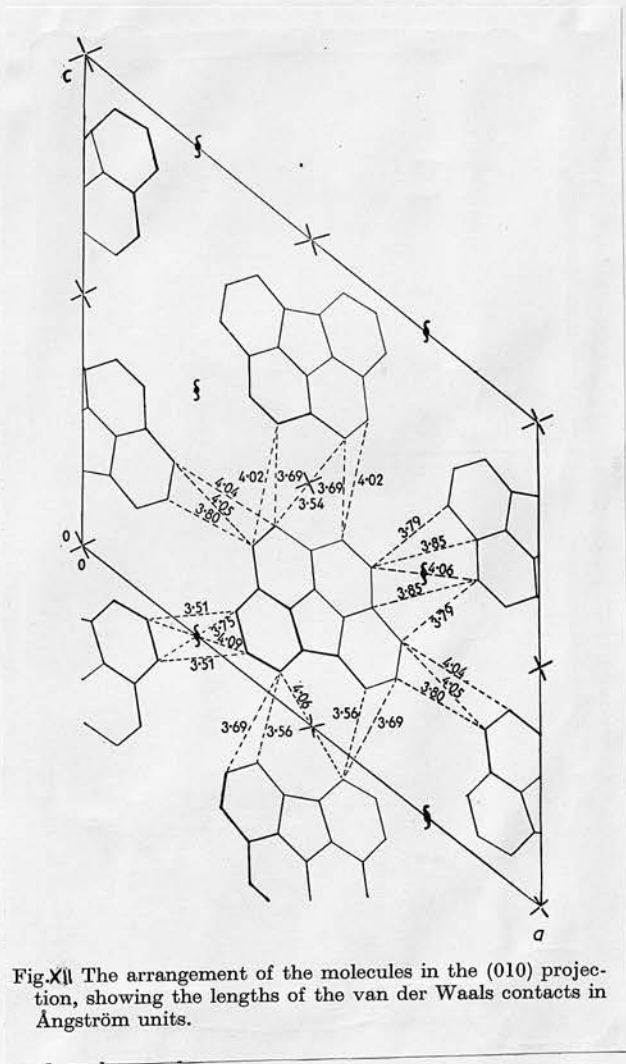


Fig.XII The arrangement of the molecules in the (010) projection, showing the lengths of the van der Waals contacts in Angstrom units.

Therefore the plane of the molecule passes through the crystallographic centre of symmetry. In this respect the structure of 2:13-Benzfluoranthene is different.

where

f_1 is the atomic scattering factor at 2θ

F is the isotropic Debye factor,

$$F = \sum_{i=1}^N \frac{f_i}{r_i^3}$$

r_i is the distance of the atom from the origin

fractions of the cell edges a, b, c .

The trigonometric part of this equation can always be reduced to an algebraic sum of products of sines, cosines, secants, tangents, cotangents and reciprocals.

Now, if we have orthogonal axes, then

$$\sin^2 \theta = \sin^2 \alpha^2 + \sin^2 \beta^2 + \sin^2 \gamma^2$$

where α, β, γ are the angles between the axes and the normal to the plane of the molecule. The angles α, β, γ can be calculated from the coordinates of the atoms in the molecule. The products of sines, cosines, secants, tangents, cotangents and reciprocals can be calculated on a calculator.

In the calculation of the reflections of 2:13-Benzfluoranthene, the atomic scattering factors were referred to the axes a, b, c , which are at right angles to one another. The angles α, β, γ are indicated by the subscripts.

$$\sin^2 \theta = \sin^2 \alpha^2 + \sin^2 \beta^2 + \sin^2 \gamma^2$$

The structure factor equation is

$$F(hkl) = \sum f_o \cdot \exp(-Bs^2) \cdot \exp[\sqrt{2}\pi i(hx+ky+lz)]$$

where

f_o is the atomic scattering factor at 0°K ,

B is the isotropic Debye factor,

$s = \sin\theta/\lambda$ and

x, y, z are the atomic coordinates as

fractions of the cell edges a, b & c.

The trigonometric part of this equation can always be reduced to an algebraic sum of products of $\cos 2\pi hx$, $\cos 2\pi ky$, $\cos 2\pi lz$, $\sin 2\pi hx$, $\sin 2\pi ky$ and $\sin 2\pi lz$.

Now, if we have orthogonal axes, then

$$4\sin^2\theta = h^2 a^{*2} + k^2 b^{*2} + l^2 c^{*2}.$$

We can therefore reduce the term, $\exp(-Bs^2)$, to the form, $\exp(Ph^2) \cdot \exp(Qk^2) \cdot \exp(Rl^2)$. Thus, for any one species of atoms, tables of $\exp(Ph^2) \cdot \cos 2\pi hx$, $\exp(Qk^2) \cdot \cos 2\pi ky$, etc. are prepared, and the products are formed and summed on a calculator.

In the calculation of $h0l$ reflections of 2:13-Benzfluoranthene, the atomic coordinates were referred to the axes \vec{a} and $(c + \frac{a}{2})$, which are at 92° to one another. The maximum error in $\sin^2\theta$ incurred by the approximation,

$$4\sin^2\theta = h^2 a^{*12} + l^2 c^{*12},$$

is $2\frac{1}{4}\%$, which can be neglected.

The two vectors, a^* and c^* , give rise to all the observed $h0l$'s, and the structure factor equation, which is

$$F(h0l) = 4 \cdot \sum f_o \cdot \exp(-Bs^2) \cdot \left[\cos 2\pi hx \cdot \cos 2\pi lz \right. \\ \left. - \sin 2\pi hx \cdot \sin 2\pi lz \right],$$

takes the form

$$F = 4 \cdot \sum f_o \left[\left[\exp(P h^2) \cdot \cos 2\pi hx \right] \cdot \left[\exp(Q k^2) \cdot \cos 2\pi ky \right] \right. \\ \left. - \left[\exp(P h^2) \cdot \sin 2\pi hx \right] \cdot \left[\exp(Q k^2) \cdot \sin 2\pi ky \right] \right],$$

which is suitable for calculation on a desk calculator. The procedure is similar for the other two projections, but in these there is no approximation involved, because the axes are orthogonal.

When the values of P and Q change after one cycle of refinement, only alterations in the one-dimensional tables of $\exp(P h^2) \cdot \cos 2\pi hx$, etc. need be made. In this way, contributions from all atoms of one species may be calculated at the same time. The amount of labour saved over the conventional method of treating atoms with the same temperature factor, as one species, is colossal.

By changing P, Q and R individually, anisotropy parallel to the crystallographic axes can also be corrected for, and this modification was used in the refinement of acenaphthene.

THE CRYSTAL STRUCTURE OF ACENAPHTHENE.

EXPERIMENTAL.

Crystal Specimens.

The crystals were obtained by allowing a solution of acenaphthene in a mixture of carbon tetrachloride and ethyl acetate to evaporate slowly. The crystals grew as long needles with almost circular cross section. Most other common solvents give crystal needles, which are very much thinner in one direction than in the other. In the latter specimens the predominant face is (010).

The crystals were colourless, and the needle axis was found to be parallel to the c axis. For photographic work, the crystals were made approximately cylindrical by scraping them with a razor blade, but for the Geiger counter work the cylinders were cut on a lathe. The crystal was mounted on a glass tube with seccotine, and was pared down with a standard cutting tool, very thin shavings being removed at each traverse. The diameters of the cylinders used varied from 0.7 mm. to 1.3 mm.

Since the crystals sublime, they were coated with collodion. This did not altogether prevent the sublimation, but its rate was reduced.

Photography and Visual Intensity Measurements.

The procedure was identical with that carried out for 2:13-Benzfluoranthene.

Geiger Counter Measurements.

Since Kitaigorodskii (1949) had used an ionisation spectrometer for recording his intensities, it was felt that, to justify any correction of his results, data at least as accurate as his would be required. Hence, after preliminary photographic work, data from Geiger counter measurements were used.

The spot profile technique previously employed in this laboratory was thought to be too tedious, and integrated intensities were obtained by sweeping through the reflexion, the total number of counts being recorded on a scaler. Cochran (1950) has pointed out that for this technique quite accurate results can be obtained if one assumes the counter to have a larger dead time. There are two ways of obtaining this apparent dead time; one is by direct measurement, and the other is by plotting out the spot profile and obtaining a constant K from it, which is the factor by which the real dead time of the counter must be multiplied to give the apparent one.

The dead time of the counter was determined as described in Cochran's paper, by using nickel foils cut from the same sheet of foil.

The foil ratio was simultaneously obtained. The difficulties experienced in this determination indicated that the profile method for determining K would be preferable. Unlike Cochran's findings, the value of K was not found to be constant.

Now in photographs of acenaphthene, a lot of X-ray background was observed, and since it was not evenly distributed over the Weissenberg photograph, it is probably due to the thermal vibrations of the atoms. The presence of this background must cause variations in K with the size of the reflexion. A calibration graph was then prepared for K against the ratio between the integrated intensity and the average background.

The experimental procedure was then as follows:- When the reflexion had been found in the Geiger counter (for this purpose a galvanometer in series with the counter was used as a rate meter), the crystal setting was moved $1\frac{1}{4}^{\circ}$ off the reflecting position. In this position the number of pulses due to the background was measured over three intervals of 100 seconds. The crystal was then rotated through its reflecting position by means of an electric motor, that had been geared down. It took 100seconds for it to traverse $2\frac{1}{2}^{\circ}$, and the total number of counts were recorded. This quantity was also measured three times, and the background was then measured at the other extreme of the sweep.

To ensure that no inaccuracy should

arise because of too high counting rates, nickel foils were placed in front of the counter, so that at no time during the sweep did the rate ever exceed 1000 counts per second.

Sources of intensity variation are due to fluctuations in X-ray tube performance, and to the crystal subliming. To correct for both of these, the maximum of a standard reflexion of the crystal was measured at frequent intervals. Provided the variation in this was not too large, the observed intensity was multiplied by the corresponding factor.

For small reflexions the value of the intensity was obtained as the difference between two quite large numbers, and was thus rather inaccurate. As it is easier to see whether a reflexion is present in a photograph, than it is to detect it in this rather clumsy manner, all the intensities for the weaker reflexions were measured by visual estimations from photographs. Although the percentage error in these intensities may be quite large, the absolute error is no larger than that for big reflexions measured by Geiger counter.

INTERPRETATION OF DATA.

Space Group and Cell Dimensions.

Photographs of acenaphthene show two sets of systematic absences, viz. $0kl$ when l is odd and $0k0$ when k is odd. The crystal is orthorhombic, and there are no space groups in this crystal class which require all these absences.

The absences $0kl$ when l is odd, indicate the presence of a c glide plane, perpendicular to a, and the $0k0$ absences a two-fold screw axis parallel to b. These symmetry elements give rise to the four equivalent points

$$\begin{array}{ll} \text{i)} & x, y, z \\ \text{ii)} & \bar{x}, y, \frac{1}{2}+z \\ \text{iii)} & \bar{x}, \frac{1}{2}+y, \bar{z} \\ \text{iv)} & x, \frac{1}{2}+y, \frac{1}{2}-z . \end{array}$$

Now i) and iv) are related by a b glide plane perpendicular to c at height $z=\frac{1}{4}$. This would give rise to additional absences, viz. $hk0$ when k is odd, a condition that does not obtain.

Hence one of these sets of absences must be due to conditions other than space group requirements. There is a very weak $0,15,0$ reflexion, which Kitaigorodskii failed to observe, but which can be seen on photographs of a fat crystal. Therefore, the $0k0$ absences are probably not space group phenomena in acenaphthene. This now gives a choice of three possible space groups, namely $Pcm2_1$, $Pc2m$ and P_{cmm}^{222} (the full symmetries

have been given to show that no further absences will arise from any other symmetry elements of the space group). Bannerjee and Sinha (1937) assumed that the space group was the one with the highest symmetry, viz. P₆mm.

Kitaigorodskii published a paper (1948) relating the symmetry of molecules to the space groups of their crystals. P₆mm is not listed among his collection of space groups, whereas P₆m is. On the strength of this he selected P₆m as the space group for acenaphthene. Since the main fault in his analysis is its inaccuracy, there was no reason to doubt his choice.

The 220 reflexion always differs in shape from the others on photographs. It is probably a double reflexion off 300 and $\bar{1}20$.

The cell dimensions were determined to a greater precision than Kitaigorodskii had done, by a procedure similar to that adopted for 2:13-Benzfluoranthene.

The Determination of the z Parameters.

The structure for acenaphthene, published by Kitaigorodskii, was considered to be essentially correct, but inaccurate. He had only solved the structure on one projection, namely onto (001), and after ascertaining that this projection did refine, the problem of solving the z parameters was undertaken.

Since a is only 8.3 Å, as compared with 14.0 Å for b, the Okl projection was chosen for the next stage. The sharpened Patterson projection was calculated from F^2 's which had been multiplied by a function $\exp(A\sin\theta)$, where A was chosen arbitrarily. The function, $\exp(A\sin\theta)$, was selected in preference to $\exp(A\sin^2\theta)$, because the latter function boosts the very high order reflexions too much relative to the others. In the transform of a molecule containing benzene rings, there are heavy regions at about $\sin\theta = 0.7$ (for Cu K_α radiation). It is therefore reasonable that a sharpening function should boost these reflexions, so that their contributions to a Patterson synthesis are not swamped by the large low order reflexions. If the function $\exp(A\sin^2\theta)$ is used, the reflexions with $\sin\theta > 0.9$ will be multiplied by a very large factor, while, if $\exp(A\sin\theta)$ is used, the effect is not so drastic for the same magnification of the ($\sin\theta = 0.7$) reflexions. The Patterson projection is shown in figure XIII.

The c axis projection had shown that there were two independent molecules, one of them (A) lying in a plane perpendicular to the c axis, and the other (B) inclined at about 28° to it. The y coordinates were known accurately, and so the problem was to find the relative z positions of the molecules, since the molecular structure was known. Superpositions were carried out, using the vectors

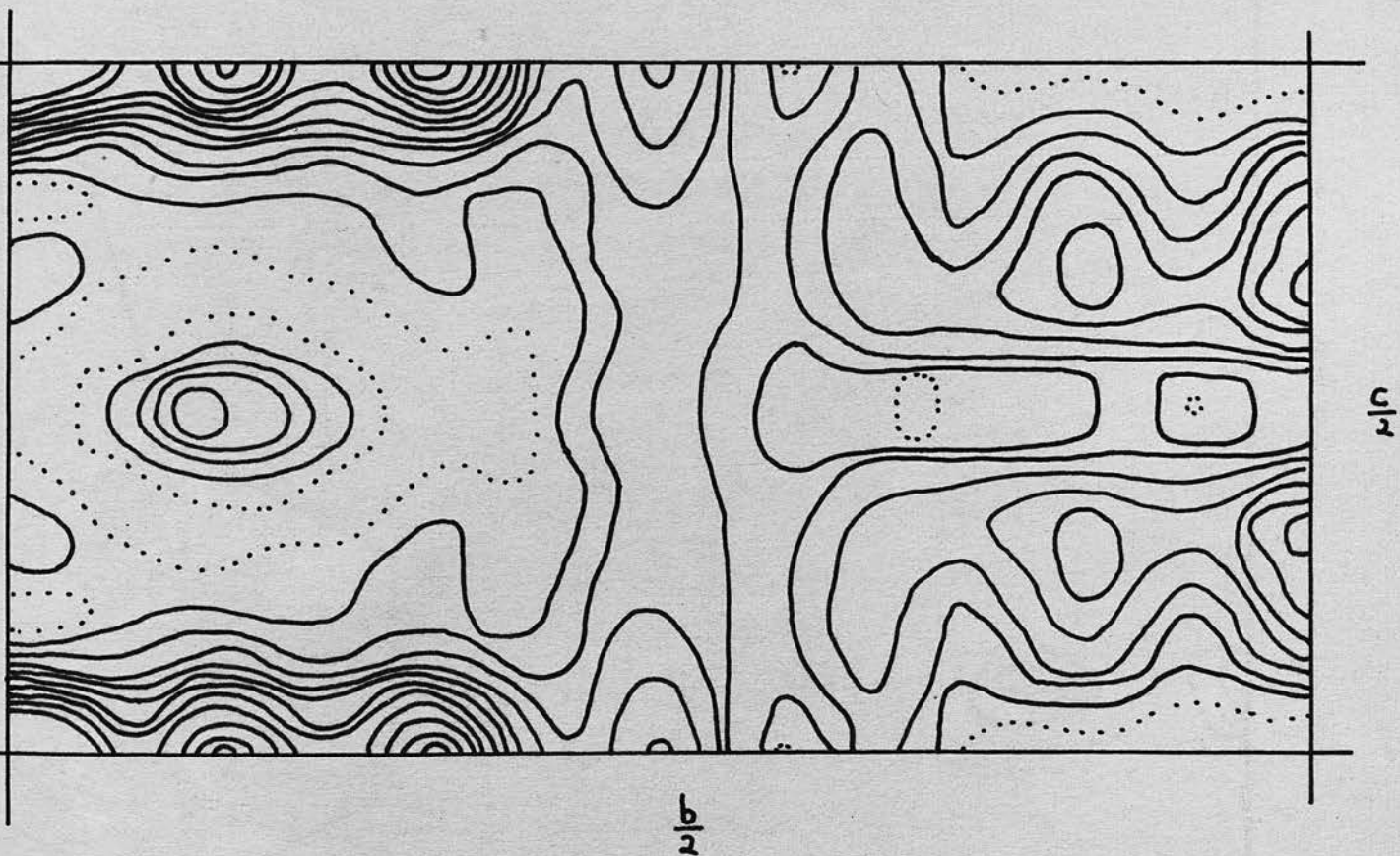


Figure XIII. The a axis Patterson projection of acenaphthene.

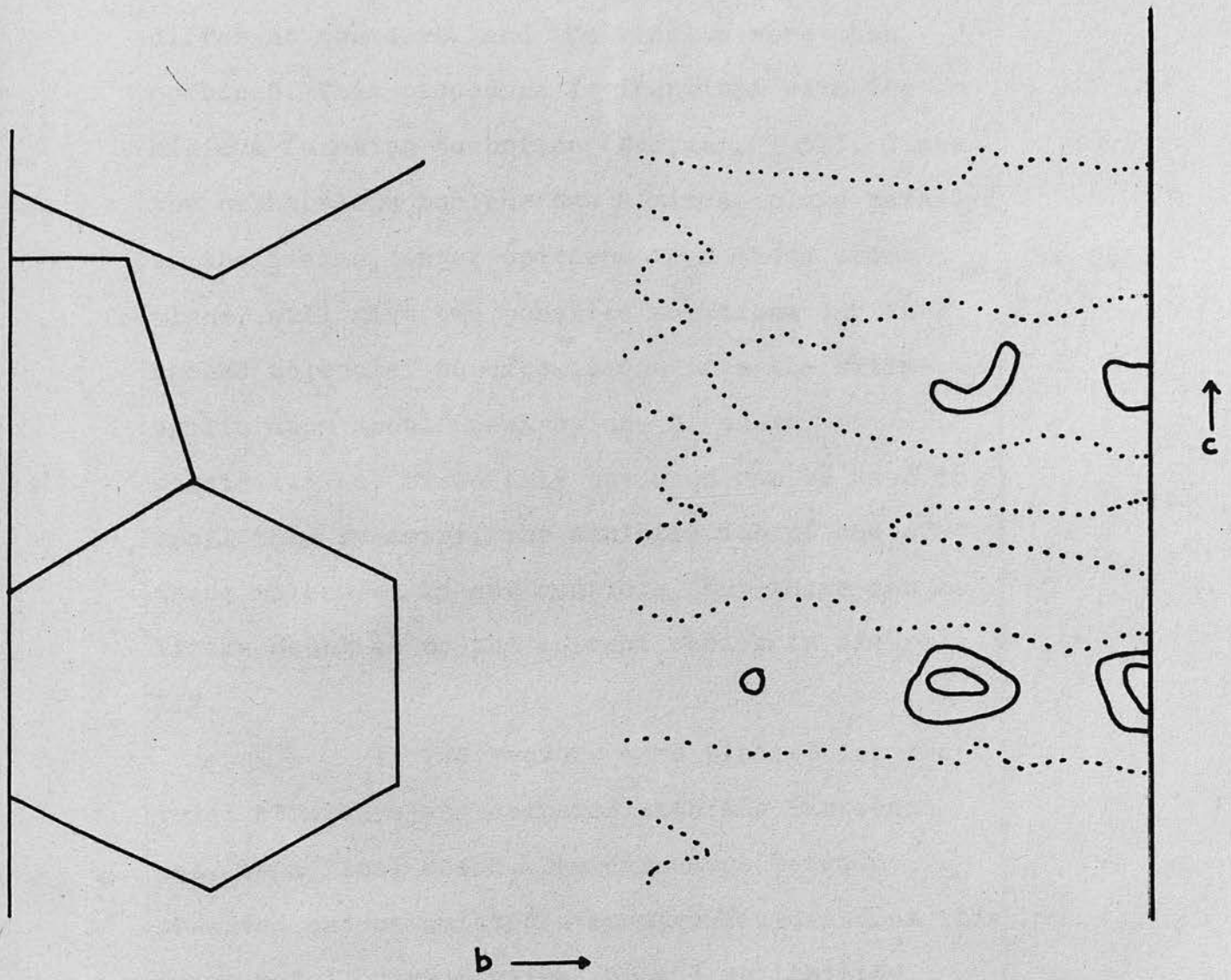


Figure XIV. The minimum function of the a axis
Patterson projection.

from the molecule whose atoms were resolved. At the known values of y , three collinear peaks should be then observable. The result is shown in figure XIV. The superposition was carried out with different contours, and the results were then combined. This procedure is identical with the minimum function technique (Buerger, 1951). Since the naphthalene nucleus has a mirror plane parallel to the b axis, superpositions from these atoms alone, will give two possible positions for the second molecule. Superpositions from the extracyclic atom should destroy one of these possibilities. Since only one atom can be used to spoil this symmetry, the annihilation of one of these molecules is not complete, but there can be little doubt as to the correct choice in figure XIV.

The vectors were plotted for the trial structure and compared with the Patterson map, as a final check. The agreement between observed and calculated structure factors from this trial model, gave a value for the reliability index, R , of 19.0.

The usefulness of the Patterson synthesis in solving structures is often underestimated. The method has the advantage that the data is presented in such a form that information from all reflexions can be used simultaneously. The method is especially useful in

solving structures containing six membered rings, because of the existence of multiple vectors in these, and, if the molecular structure is known, little difficulty should be encountered in elucidating the crystal structure.

Refinement of the Structure.

Again difference syntheses were the sole implements of refinement. The structure obtained by placing atoms to fit the (001) electron density projection published by Kitaigorodskii, was refined using F_o 's determined photographically. In the first difference map a large shift of atom C7 (see figure XVI for the numbering of the atoms) was indicated, and also high ground was observed where hydrogen atoms were to be expected. The F_c 's then included contributions from hydrogen atoms as well, and the subsequent difference map showed that there was considerable anisotropy in the thermal vibrations of the atoms. This was corrected for by the procedure already described.

The fifth difference map showed that little improvement could be expected from further refinement of the photographically obtained data, and Geiger counter measurements were then used. The F_o 's of weak reflexions and those whose $\sin\theta > 0.845$, were still obtained from the photographs, however. Corrections for

secondary extinction were applied, the extinction coefficient being found by trial. It was felt that at this stage of the analysis, this step was permissible. After sixteen stages the refinement was considered complete, as far as the corrections employed were concerned. The remaining electron density detail can be explained by the assumption that the anisotropic vibration is not exactly parallel to the crystallographic axes for some of the atoms, namely A2, A3, B2 and B3. These are the atoms which would not be vibrating parallel to the crystal axes, if the molecule as a whole, has rotational oscillation about an axis perpendicular to the plane of the molecule. The temperature factors of the various atoms are generally consistent with this hypothesis.

The final value of R (as previously defined) for the (001) projection was 9.2, when unobserved reflexions were considered as having $F_o = 0$. When, however, the value of $F_o = \frac{\sqrt{2}}{2} \cdot (\text{minimum observed})$ was used, R dropped to 7.8.

The other two projections were also refined by difference syntheses, but only the z parameters were adjusted at each stage, since the x and y parameters were more accurately determinable from the centrosymmetric (001) projection. Fortunately, there are no indications of x and y shifts in the final difference syntheses.

For these projections, photographically measured data were used, again with arbitrary extinction corrections. Since resolution of the atoms is poor, and since there is no centre of symmetry in these projections, it was not considered worth while to get accurate intensities by Geiger counter measurements, as, under these conditions, the danger of over-refinement is appreciable.

When the refinement was considered complete (the value of R for both projections was 8.3), the dimensions of the two molecules were calculated. The agreement between equivalent bond lengths was rather discouraging, although the differences were not significant. Molecule A had always been planar throughout the refinement, and the mean plane through molecule B was found by least squares. The deviations from this plane were not significant, the maximum displacement being 0.007 Å, which is very small considering that the standard error in the atomic position was about 0.032 Å. The z coordinates were then adjusted, to the nearest $\frac{c}{1000}$, giving the best fit onto the mean plane. The agreement in bond lengths between the two molecules showed marked improvement, and so the structure factors for this adjusted structure were calculated. Better agreement between $|F_c|$ and $|F_o|$ was obtained, that is $\Sigma(|F_c| - |F_o|)^2$ became smaller for both projections, but $\Sigma 1^2(|F_c| - |F_o|)^2$

increased. Neither were the difference maps any help in deciding between the structures. On chemical, as distinct from crystallographic grounds, the second structure was therefore preferred. The final values of R for the h0l and 0kl projections were 8.1 and 8.5 respectively, regarding unobserved reflexions as having $|F_o| = 0$. Correcting for these reflexions as before, however, these values became 8.0 and 7.6 respectively.

DETAILS OF THE ANALYSIS.

Cell Dimensions and Space Group.

At 15°C

$$a = 8.290 \pm 0.004 \text{ \AA}$$

$$b = 14.000 \pm 0.007 \text{ \AA}$$

$$c = 7.225 \pm 0.004 \text{ \AA}$$

$$\text{Cell volume} = 838.5 \pm 1.3 \text{ \AA}^3$$

$$\text{Density calc.} = 1.22 \text{ g/cc.}$$

$$\text{obs.} = 1.19 \text{ g/cc. (Merck Index).}$$

Space Group (as determined by Kitaigorodskii) - Pcm (C_{2v}^2)

$$Z = 4.$$

Atomic Coordinates.

The f_0 curve for carbon that was used, was again that of Hoerni & Ibers.

The hydrogen atom scattering factor curve was obtained from the International Tables. This time the positions of the hydrogen atoms were also refined, and the Debye factor, B, for these atoms was taken as 5.5 \AA^2 .

The atomic parameters are listed in the table on the following page.

Parameters of the Carbon Atoms.

Atom	x	y	z	B _x	B _y	B _z
A1	0.460	0.4165	0.000	4.3	3.9	2.0
A2	0.383	0.3295	0.000	4.7	4.3	3.7
A3	0.210	0.3280	0.000	4.8	4.5	3.7
A4	0.123	0.4090	0.000	3.0	6.8	3.7
A5	0.196	0.5000	0.000	3.5	4.3	3.7
A6	0.365	0.5000	0.000	3.7	3.0	3.0
A7	0.638	0.4450	0.000	2.5	4.7	2.5
B1	0.288	0.0835	0.675	2.7	3.5	2.0
B2	0.252	0.1705	0.599	4.5	4.5	4.0
B3	0.171	0.1720	0.428	4.3	4.1	3.0
B4	0.127	0.0910	0.335	3.2	6.0	2.7
B5	0.165	0.0000	0.415	3.0	4.1	4.0
B6	0.244	0.0000	0.582	2.7	4.0	2.3
B7	0.371	0.0550	0.850	6.8	5.0	4.6

Coordinates of the Hydrogen atoms.

Atom	120x	120y	120z
A2	53	32	0
A3	21	31	0
A4	1	49	0
A7	83	50	13
A7'	83	50	107
B2	31	28	75
B3	17	29	45
B4	9	11	30
B7	57	10	102
B7'	41	10	118

Structure Factors.

The calculated and observed structure factors are shown in the following table.

hkl	F _c	F _o	hkl	F _c	F _o
000	328.0	-	290	0.5	0.9
010	0.0	<0.2	2,10,0	-2.1	2.0
020	64.8	67.3	2,11,0	-9.4	9.2
030	-0.2	<0.3	2,12,0	-10.5	10.8
040	-23.0	23.7	2,13,0	-5.9	5.7
050	-0.6	<0.5	2,14,0	0.9	1.9
060	1.5	<0.5	2,15,0	1.0	0.9
070	-0.5	<0.6	2,16,0	-1.8	2.8
080	-26.4	26.1	2,17,0	1.3	<0.5
090	0.0	<0.7			
0,10,0	9.4	9.2	300	-19.2	18.5
0,11,0	0.6	<0.8	310	-3.6	4.4
0,12,0	29.0	28.7	320	13.3	13.3
0,13,0	0.1	<0.9	330	2.1	1.1
0,14,0	0.6	<0.9	340	5.8	5.7
0,15,0	-0.6	2.0	350	-17.6	18.2
0,16,0	1.6	1.4	360	-8.6	8.3
0,17,0	-0.7	<0.6	370	-11.6	11.3
0,18,0	4.6	4.6	380	-6.8	7.6
			390	2.0	1.5
100	-24.0	23.5	3,10,0	-10.1	10.3
110	30.0	28.9	3,11,0	-0.2	0.9
120	-20.2	18.8	3,12,0	-8.3	7.7
130	-10.1	10.5	3,13,0	1.1	1.8
140	-6.0	6.3	3,14,0	1.7	1.6
150	7.4	7.5	3,15,0	0.1	<0.7
160	7.5	7.2	3,16,0	1.5	1.8
170	1.4	<0.6	3,17,0	-3.8	4.2
180	12.7	13.3			
190	-2.0	1.6	400	-26.5	27.1
1,10,0	7.5	7.6	410	12.2	12.6
1,11,0	7.3	7.4	420	-17.2	17.4
1,12,0	0.4	<0.9	430	-2.2	1.6
1,13,0	3.8	3.9	440	0.9	<0.7
1,14,0	-2.3	2.4	450	8.5	8.4
1,15,0	-0.8	1.0	460	8.8	9.5
1,16,0	-1.1	1.4	470	4.7	5.2
1,17,0	0.9	1.3	480	4.6	3.5
			490	-2.0	2.0
200	-69.0	68.3	4,10,0	2.6	3.1
210	-34.7	33.8	4,11,0	3.4	2.6
220	0.9	-	4,12,0	2.2	2.0
230	9.1	9.4	4,13,0	2.4	2.3
240	-7.1	6.8	4,14,0	0.5	<0.8
250	6.4	7.3	4,15,0	0.2	<0.7
260	-30.5	29.1	4,16,0	-1.5	<0.5
270	6.8	7.5			
280	3.3	2.1	500	8.4	8.4

hkl	F _c	F _o	hkl	F _c	F _o
510	-10.3	11.2	770	0.1	<0.9
520	-5.8	5.2	780	1.2	2.4
530	5.0	5.3	790	-2.4	2.4
540	12.7	12.6	7,10,0	5.0	4.7
550	-2.7	1.9	7,11,0	4.6	4.5
560	27.2	27.2	7,12,0	2.6	1.4
570	-0.6	1.6	7,13,0	3.0	3.1
580	-1.4	<0.9			
590	1.8	1.9	800	11.3	11.3
5,10,0	-5.4	5.1	810	-0.8	<0.9
5,11,0	-4.8	3.7	820	4.8	5.0
5,12,0	0.8	<0.8	830	0.7	<0.9
5,13,0	-2.6	2.7	840	-1.9	1.1
5,14,0	-1.8	2.5	850	1.1	<0.8
5,15,0	0.7	0.6	860	-2.0	1.9
5,16,0	3.7	3.6	870	1.5	2.6
			880	-2.3	2.6
600	4.3	4.1	890	2.0	1.1
610	-4.2	4.6	8,10,0	-0.3	<0.6
620	5.4	5.5	8,11,0	0.8	<0.5
630	-4.7	4.6	8,12,0	0.9	1.2
640	3.0	2.6			
650	0.0	<0.9	900	-1.4	<0.8
660	-0.8	<0.9	910	-5.4	6.0
670	0.4	<0.9	920	0.7	<0.8
680	0.0	1.8	930	0.8	<0.8
690	-0.9	<0.9	940	-1.7	2.1
6,10,0	0.0	<0.9	950	1.5	1.8
6,11,0	0.1	<0.8	960	-3.8	4.2
6,12,0	-0.3	0.7	970	1.9	2.0
6,13,0	-0.9	1.3	980	0.9	<0.5
6,14,0	0.7	<0.5	990	0.6	<0.4
700	-0.5	<0.9	10,0,0	-2.8	2.5
710	12.4	11.8	10,1,0	0.1	<0.6
720	-1.2	<0.9	10,2,0	-2.4	2.1
730	-0.5	<0.9	10,3,0	1.7	1.2
740	-7.6	8.7	10,4,0	-1.9	0.9
750	3.1	3.4	10,5,0	-5.5	5.3
760	-10.4	9.0	10,6,0	-1.1	0.9

hkl	A _c	B _c	F _c	F _o
101	21.3	-4.6	21.8	20.7
201	-49.3	-20.5	53.4	49.4
301	-23.2	37.1	43.8	40.7
401	12.9	-17.4	21.7	23.1
501	13.7	2.1	13.9	14.6
601	1.9	4.9	5.3	5.3
701	-3.4	0.5	3.4	4.3
801	0.8	-7.4	7.4	9.2
901	-0.6	-2.6	2.6	2.8
10,0,1	-2.5	2.9	3.8	3.1
002	110.5	-17.1	111.8	113.4
102	-20.3	-11.7	23.4	25.3
202	-13.4	-22.0	25.8	27.1
302	-17.2	20.9	27.1	29.2
402	-13.9	33.9	36.6	33.8
502	19.4	-7.6	20.8	21.0
602	5.0	-13.4	14.3	13.6
702	-10.3	0.4	10.3	11.1
802	4.9	0.5	4.9	4.5
902	1.9	-0.2	1.9	3.0
10,0,2	-3.1	0.4	3.1	4.0
103	3.1	46.7	46.8	46.5
203	-15.2	20.5	25.5	27.2
303	-9.0	0.8	9.0	11.6
403	8.3	-9.9	12.9	14.3
503	13.0	5.7	14.2	13.2
603	1.6	-14.0	14.1	15.3
703	-8.7	-2.1	8.9	10.0
803	-3.7	1.1	3.9	3.6
903	3.1	-0.3	3.1	4.0
10,0,3	2.3	2.6	3.5	3.6
004	24.6	0.3	24.6	25.1
104	-12.9	-1.6	13.0	12.7
204	10.9	4.6	11.8	13.3
304	-2.4	1.8	3.0	2.9
404	-11.2	-1.5	11.3	10.2
504	8.3	-0.1	8.3	10.7
604	3.6	-7.0	7.9	6.7
704	-8.4	-3.8	9.2	11.1
804	1.4	7.5	7.6	10.1
904	2.9	5.1	5.9	7.6
105	-7.4	22.9	24.1	22.8
205	-7.0	8.3	10.9	10.9
305	2.3	-0.5	2.4	<1.1
405	-0.1	-17.1	17.1	15.0
505	1.5	4.4	4.7	4.6
605	-1.9	2.2	2.9	2.2
705	-4.0	0.1	4.0	3.5
805	-2.9	-2.2	3.6	2.8
905	2.5	1.6	3.0	2.9



hkl	A _c	B _c	F _c	F _o
006	27.9	0.2	27.9	25.4
106	-11.0	-2.2	11.2	12.4
206	3.1	1.5	3.4	4.1
306	4.3	2.9	5.2	4.1
406	-12.2	-1.7	12.3	13.2
506	-2.2	-1.2	2.5	2.4
606	1.7	0.2	1.7	2.1
706	-1.5	0.3	1.5	3.3
806	4.2	0.0	4.2	4.9
107	-0.1	13.6	13.6	13.1
207	-4.6	2.3	5.1	3.3
307	-1.1	0.8	1.4	2.0
407	2.4	-9.9	10.2	9.9
507	-0.3	1.8	1.8	1.7
607	-0.7	1.1	1.3	2.2
707	3.1	1.3	3.4	1.9
008	8.8	-3.2	9.4	9.2
108	-7.0	-0.2	7.0	6.3
208	4.1	0.4	4.1	2.7
308	0.8	0.3	0.9	1.8
408	-4.4	0.8	4.5	3.6
508	4.1	-0.1	4.1	4.1
109	-1.0	7.4	7.5	5.3
209	1.4	3.7	4.0	2.1
012	-85.1	-15.9	86.6	85.8
022	10.4	-12.5	16.3	16.3
032	2.6	-7.1	7.6	7.5
042	1.7	-0.6	1.8	2.4
052	20.2	4.4	20.7	23.5
062	26.2	5.7	26.8	29.5
072	19.2	4.5	19.7	21.7
082	-7.9	3.1	8.5	7.8
092	5.3	2.4	5.8	6.5
0,10,2	3.2	2.5	4.1	3.5
0,11,2	-10.9	2.7	11.2	11.0
0,12,2	14.2	2.7	14.5	15.9
0,13,2	-6.6	2.2	7.0	7.6
0,14,2	-0.7	1.1	1.3	<1.5
0,15,2	0.6	-0.1	0.6	<1.4
0,16,2	2.6	-1.0	2.8	3.8
0,17,2	-0.2	-1.5	1.5	<1.0
014	-57.6	1.9	57.6	57.5
024	6.1	4.6	7.6	10.1
034	5.9	4.8	7.6	7.5
044	-3.3	1.9	3.8	2.4
054	-3.9	-1.1	4.1	5.6
064	0.9	-1.7	1.9	<1.4
074	4.8	0.2	4.8	4.3
084	-3.5	1.7	3.9	4.9
094	8.5	1.1	8.6	8.8

h k l	A _c	B _c	F _c	F _o
0,10,4	2.2	-1.1	2.5	3.1
0,11,4	-12.9	-2.8	13.2	15.0
0,12,4	5.2	-2.9	6.0	7.2
0,13,4	-7.2	-1.6	7.4	8.4
0,14,4	0.4	-0.2	0.4	<1.2
0,15,4	1.0	0.5	1.1	2.9
0,16,4	0.5	0.6	0.8	<0.7
016	-17.1	1.9	17.2	15.3
026	13.4	4.8	14.2	14.6
036	4.9	4.8	6.9	6.1
046	-8.3	1.0	8.4	7.4
056	-15.3	-3.5	15.7	15.3
066	-16.5	-5.0	17.2	15.9
076	-8.7	-2.9	9.2	10.2
086	-8.5	0.2	8.5	9.3
096	4.4	1.3	4.6	4.9
0,10,6	2.1	0.3	2.1	2.4
0,11,6	-7.7	-1.0	7.8	9.7
0,12,6	5.2	-0.9	5.3	5.0
0,13,6	-3.5	0.3	3.5	3.7
018	-16.9	-2.6	17.1	15.5
028	2.9	-1.3	3.2	2.5
038	1.3	-0.2	1.3	<1.2
048	-0.2	0.1	0.2	<1.2
058	1.2	-0.1	1.2	<1.1
068	0.2	0.2	0.3	<1.1
078	2.8	0.0	2.8	3.6
088	-2.7	0.3	2.7	<0.8
098	2.0	0.4	2.0	1.6

Molecular Dimensions.

Molecule A lies on the plane $z = 0$, and molecule B on the plane $2.112x + 0.0666 = z$, where x and z are the fractional coordinates of the atoms referred to crystal axes a and c. These two planes make angles of 0° and $61\frac{1}{2}^\circ$ to the (001) plane. The displacement of the hydrogen atoms from the planes are shown in the table on the next page. The maximum displacement of a carbon atom from its appropriate plane is 0.001 \AA .

Hydrogen atom	Displacement from the plane (\AA)	
	Molecule A	Molecule B
2	0	- 0.044
3	0	- 0.032
4	0	- 0.086
7	+ 0.783	+ 0.759
7'	- 0.783	- 0.673

The individual bond lengths and angles are shown in figure XV, and the weighted means of the values for chemically identical bonds are shown in figure XVI.

Estimation of Accuracy.

The standard deviations of the electron density and the atomic coordinates were again calculated by the method of Cruickshank. The results are

$\sigma(x) = \sigma(y) = 0.010 \text{ \AA}$, $\sigma(z) = 0.030 \text{ \AA}$ for a carbon atom,

$\sigma(x) = \sigma(y) = 0.11 \text{ \AA}$, $\sigma(z) = 0.33 \text{ \AA}$ for a hydrogen atom,

$\sigma(\rho) = 0.36 \text{ e.\AA}^{-2}$ for the (100) projection,

$\sigma(\rho) = 0.79 \text{ e.\AA}^{-2}$ for the (010) projection, and

$\sigma(\rho) = 0.13 \text{ e.\AA}^{-2}$ for the (001) projection.

The value for $\sigma(\rho)$ in the (010) projection is so large, because there is a mirror plane parallel to (010), thus doubling the electron density in this projection.

The standard deviations of the bond lengths and angles may be calculated from these figures.

The standard deviation of a bond length, d , between atoms 1 and 2 is calculated from

$$\begin{aligned}\sigma^2(d) = & \left[\sigma^2(x_1) + \sigma^2(x_2) \right] \cos^2 p \\ & + \left[\sigma^2(y_1) + \sigma^2(y_2) \right] \cos^2 q \\ & + \left[\sigma^2(z_1) + \sigma^2(z_2) \right] \cos^2 r ,\end{aligned}$$

where $\cos p$, $\cos q$ and $\cos r$ are the direction cosines of the bond relative to \underline{a} , \underline{b} and \underline{c} , the crystal axes (see Ahmed & Cruickshank, 1953). Now, since in this case $\sigma(x) = \sigma(y)$,

$$\begin{aligned}\sigma^2(d) = & \left[\sigma^2(x_1) + \sigma^2(x_2) \right] \left[\cos^2 p + \cos^2 q \right] \\ & + \left[\sigma^2(z_1) + \sigma^2(z_2) \right] \cos^2 r .\end{aligned}$$

Furthermore, one of the properties of direction cosines is that

$$\cos^2 p + \cos^2 q + \cos^2 r = 1 ,$$

and therefore

$$\begin{aligned}\sigma^2(d) = & \left[\sigma^2(x_1) + \sigma^2(x_2) \right] \sin^2 r \\ & + \left[\sigma^2(z_1) + \sigma^2(z_2) \right] \cos^2 r .\end{aligned}$$

The standard deviation of the angle, ϕ , at atom 2 between bonds of length d and e , is given by the equation

$$\begin{aligned}\sigma^2(\phi) = & \frac{1}{(d \cdot e \cdot \sin \phi)^2} \left[\begin{aligned} & (x_2 - x_3)^2 \sigma^2(x_1) \\ & + (x_1 - 2x_2 + x_3)^2 \sigma^2(x_2) \\ & + (x_2 - x_1)^2 \sigma^2(x_3) \\ & + \text{similar terms in } y \text{ and } z \end{aligned} \right] \end{aligned}$$

The best mean of several quantities x_j , each with a standard deviation σ_j , is

$$\frac{\Sigma(x_j/\sigma_j^2)}{\Sigma(1/\sigma_j^2)}$$

and the standard deviation of this mean is given by

$$\sigma^2(\text{mean}) = \frac{1}{\Sigma(1/\sigma_j^2)} .$$

From these equations, the values of the standard deviations shown in the diagrams were derived.

Fourier Syntheses.

The final F_o syntheses onto(100), (010) and (001) are shown in figures XVII, XVIII and XIX respectively.

The $(F_o - F_c)$ syntheses with F_c only including contributions from carbon atoms, are shown in figures XX, XXI and XXII. This means that the phases of the difference terms for the $F(h0l)$'s and $F(0kl)$'s need not be correct. In the $F(hk0)$'s the phase angle can only be 0 or π , and there is no doubt about the phase angles of all but a few reflexions.

McGeachin (1956) found that in the non-centrosymmetric projection of α -rhamnose monohydrate, the hydrogen atom peaks were poor, when the phases of the reflexions were calculated from the contributions of the heavy atoms alone.

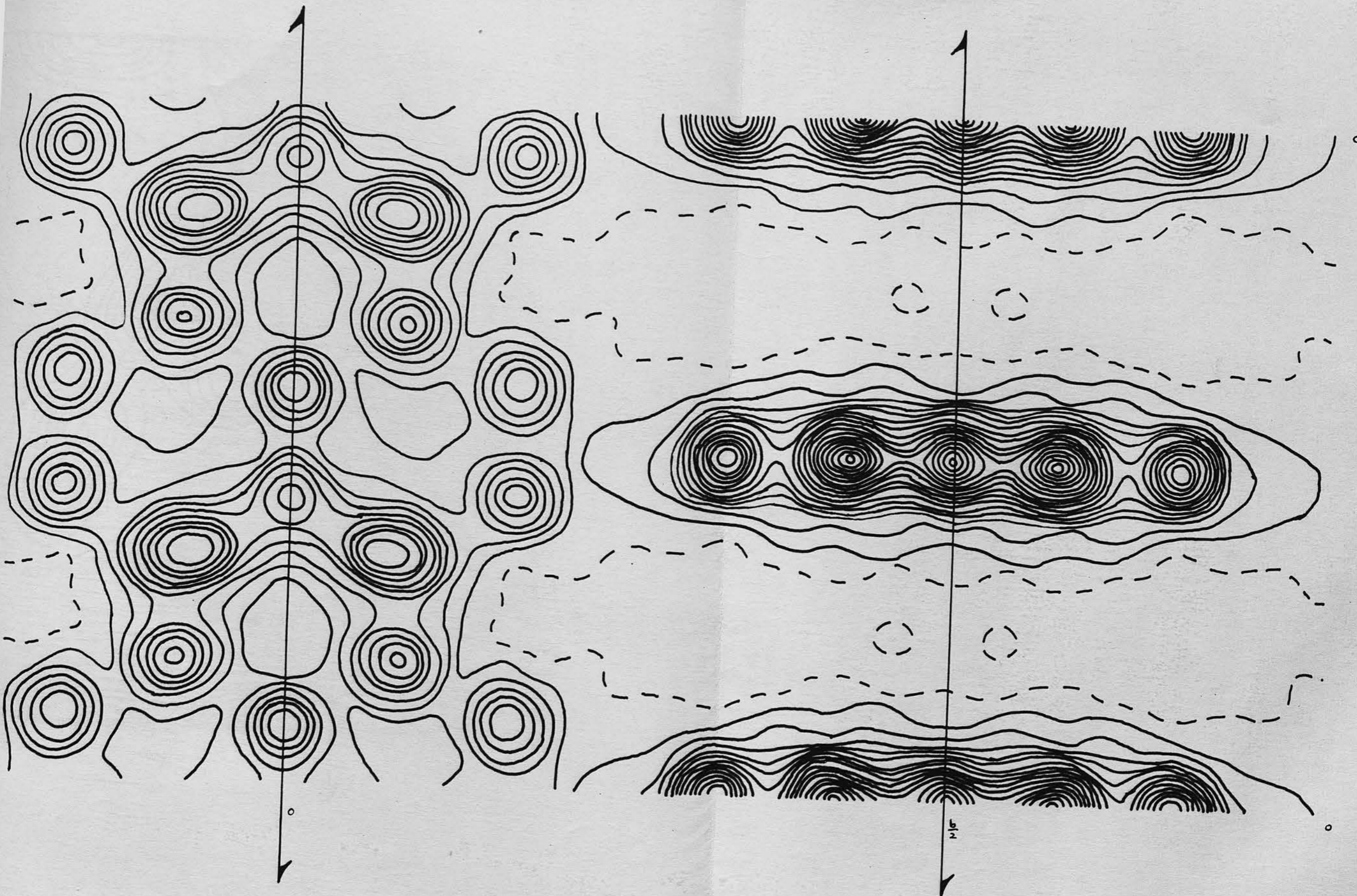


Figure XVII. The F_0 synthesis for the $F(0kl)$'s of acenaphthene. Contours every $1 \text{ e.}\text{\AA}^{-2}$, the $1 \text{ e.}\text{\AA}^{-2}$ contour being broken.

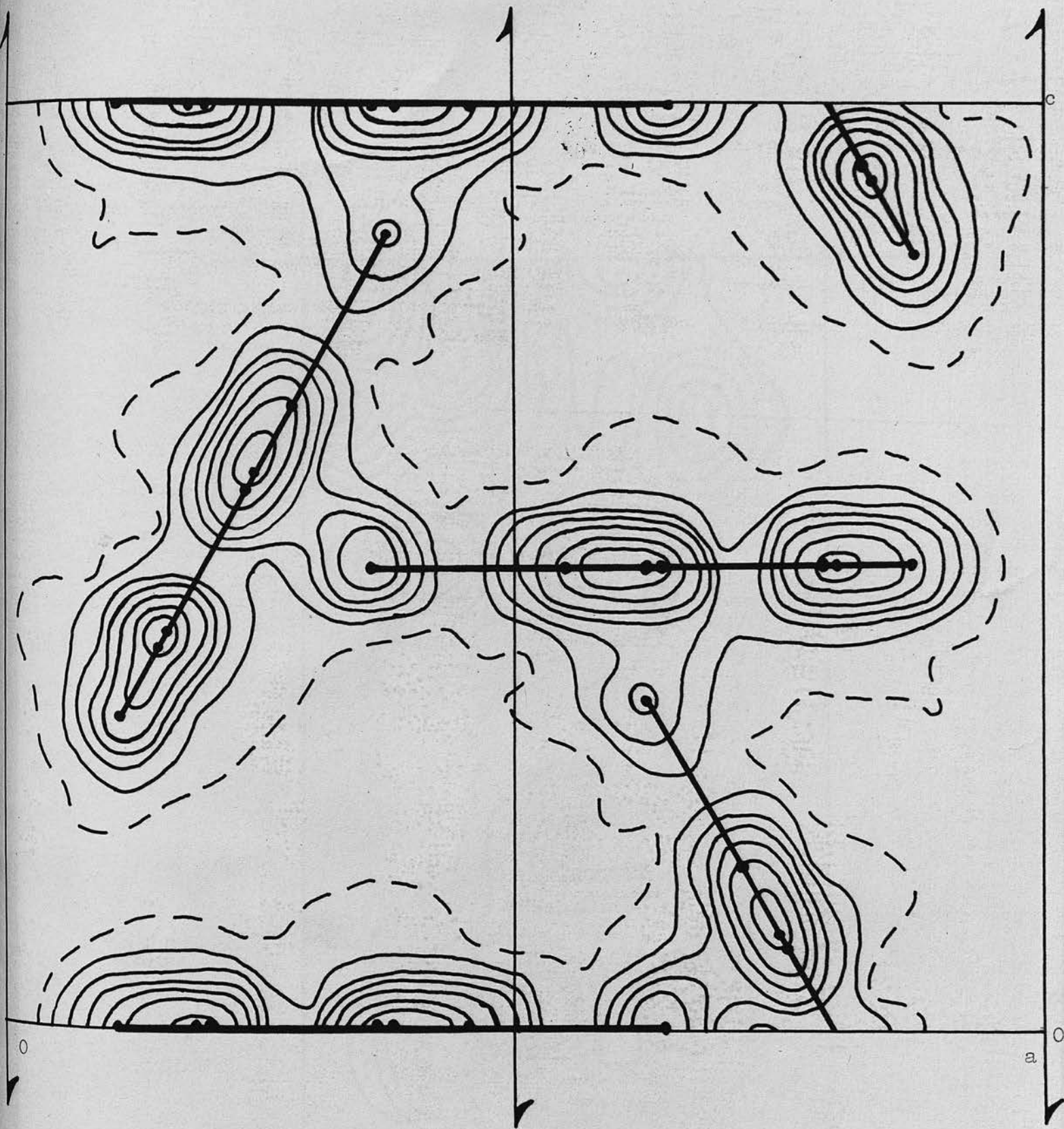


Figure XVIII. The F_0 synthesis for the $F(h0l)$'s of acenaphthene.

Contours every 3 $e.\text{\AA}^{-2}$, the 3 $e.\text{\AA}^{-2}$ contour being broken.

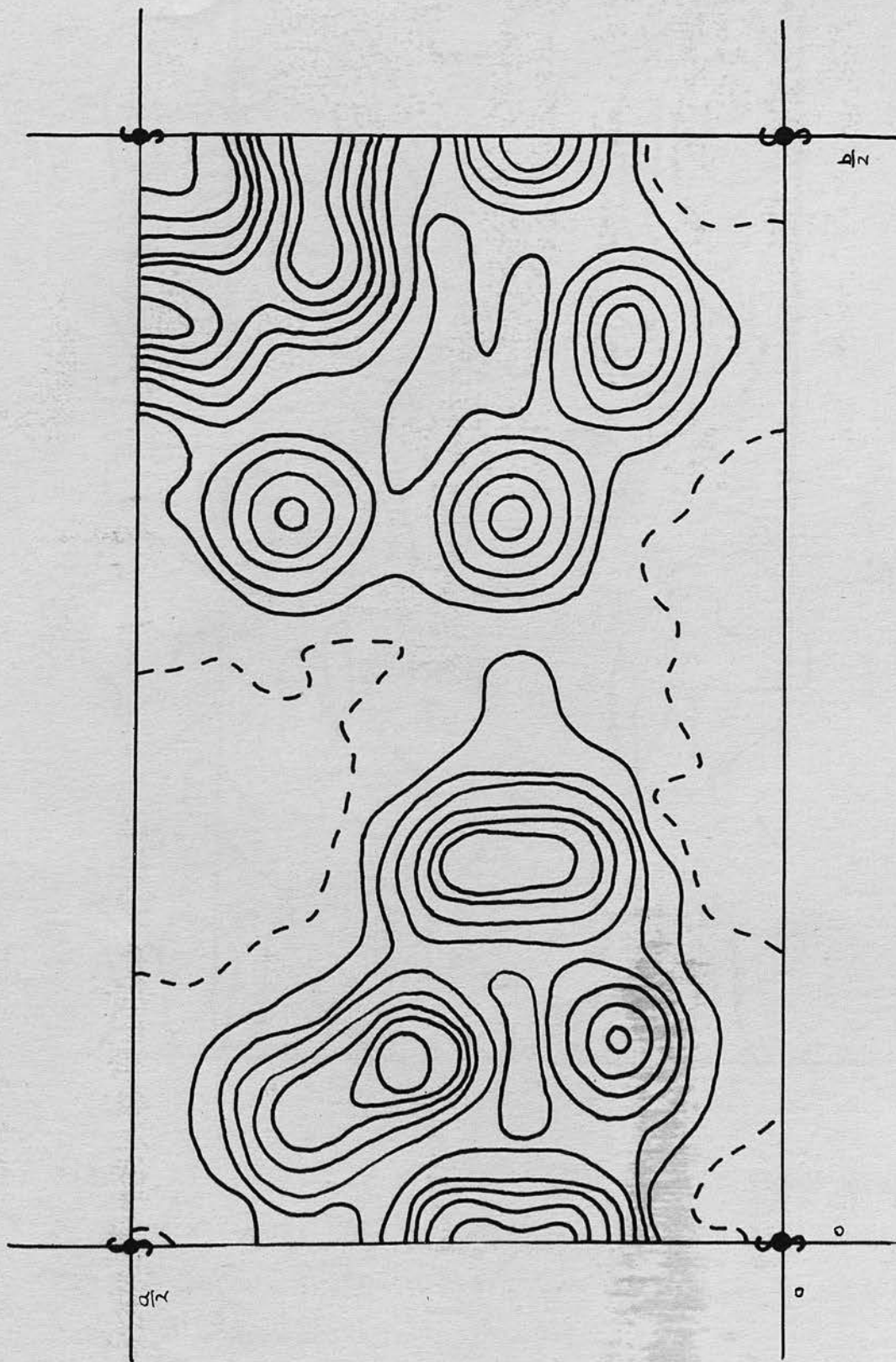


Figure XIX. The F_0 synthesis for the $F(hk0)$'s of acenaphthene. Contours every $1e.\text{\AA}^{-2}$, the $1e.\text{\AA}^{-2}$ one being broken.

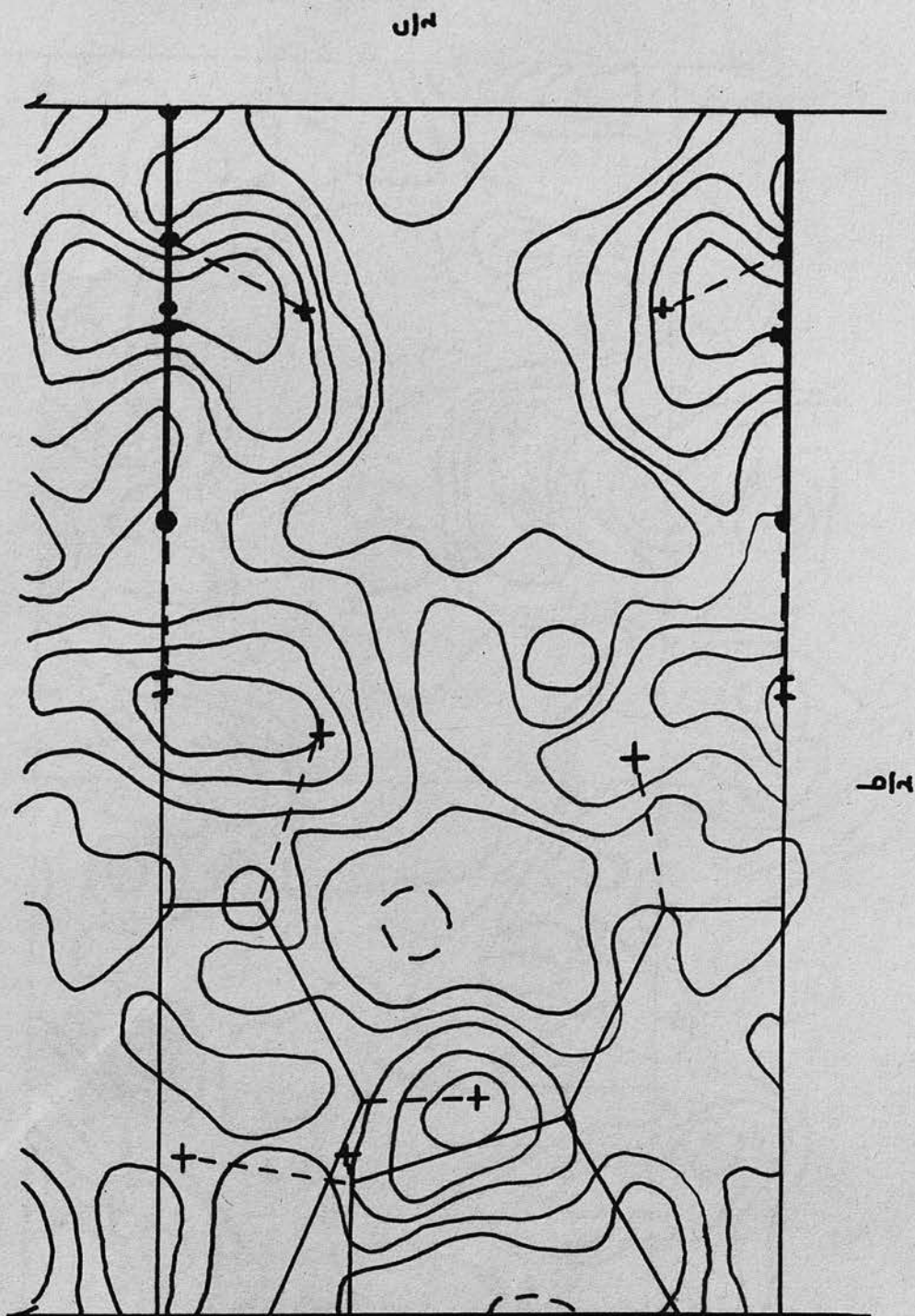


Figure XX. The $(F_o - F_c)$ synthesis for the (100) projection of acenaphthene. The F_c 's only include the carbon atom contributions. Contours every $0.2 \text{ e.}\text{\AA}^{-2}$, the negative contours being broken.

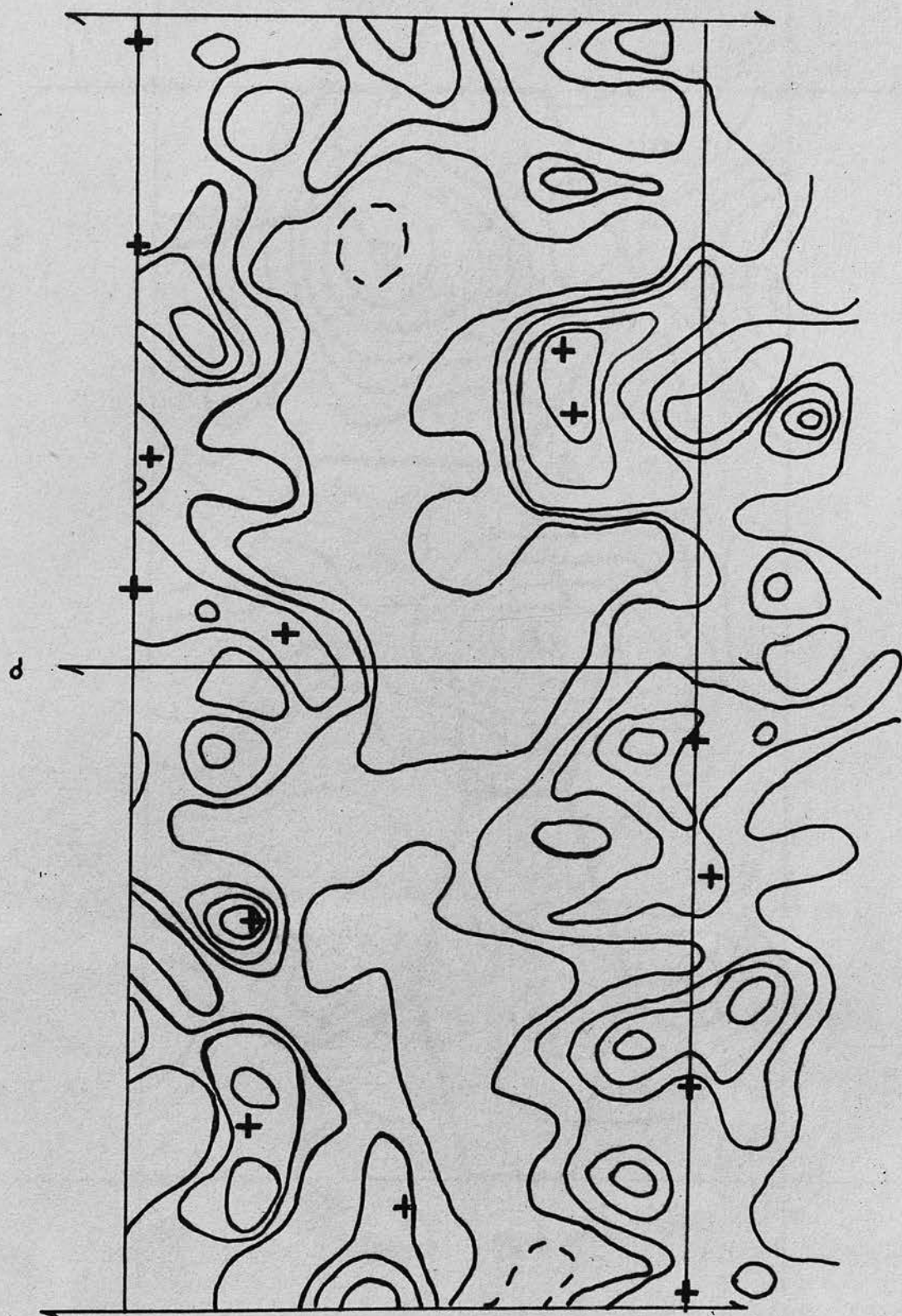


Figure XXI. The $(F_o - F_c)$ synthesis for the (010) projection of acenaphthene. Contour scales is twice that of figure XX. The F_c 's only include carbon atom contributions.

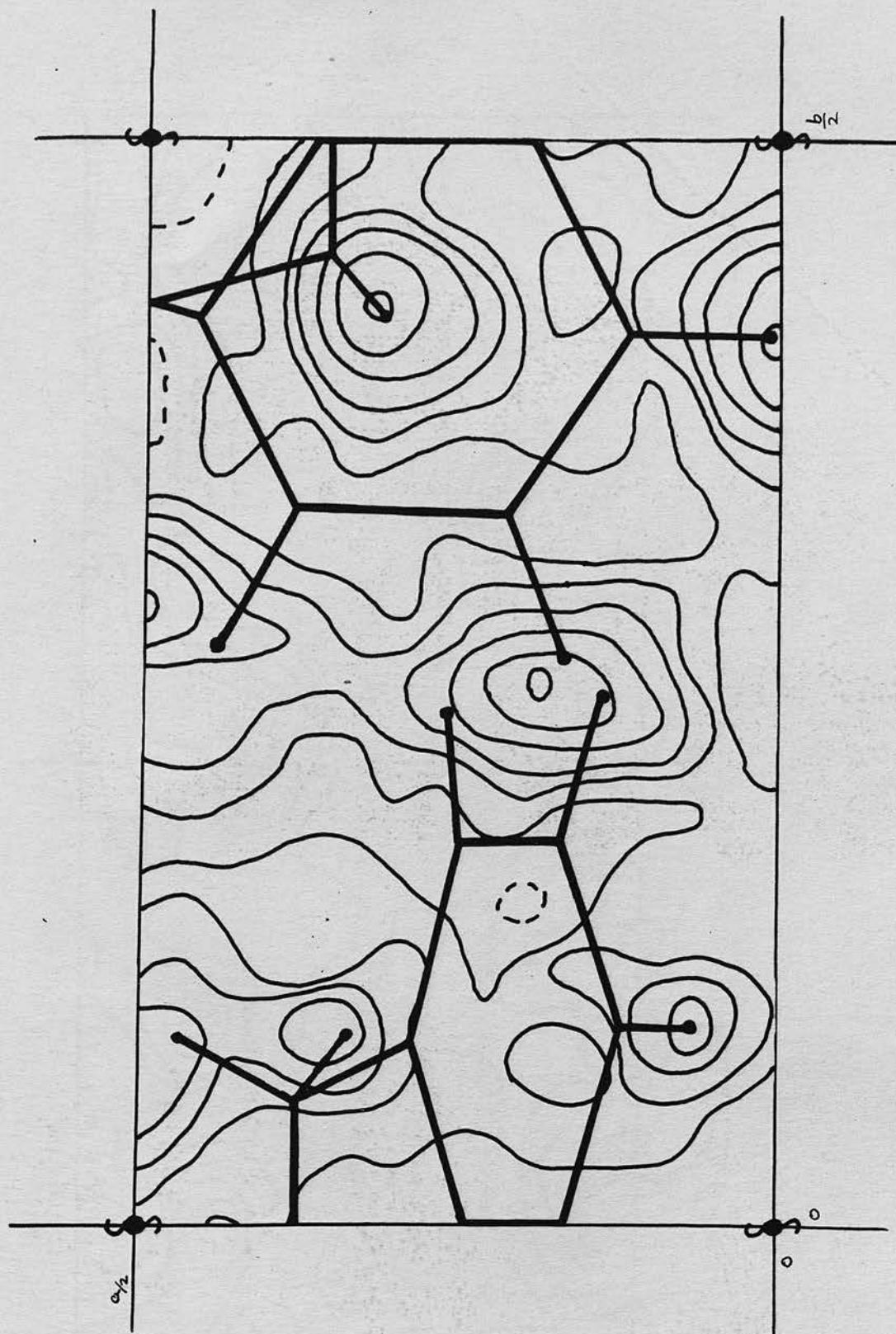


Figure XXIII. The $(F_o - F_c)$ synthesis for the $F(hk0)$'s of acenaphthene, the F_c 's only including the carbon atom contributions. Contour scale as in figure XX.

ulr

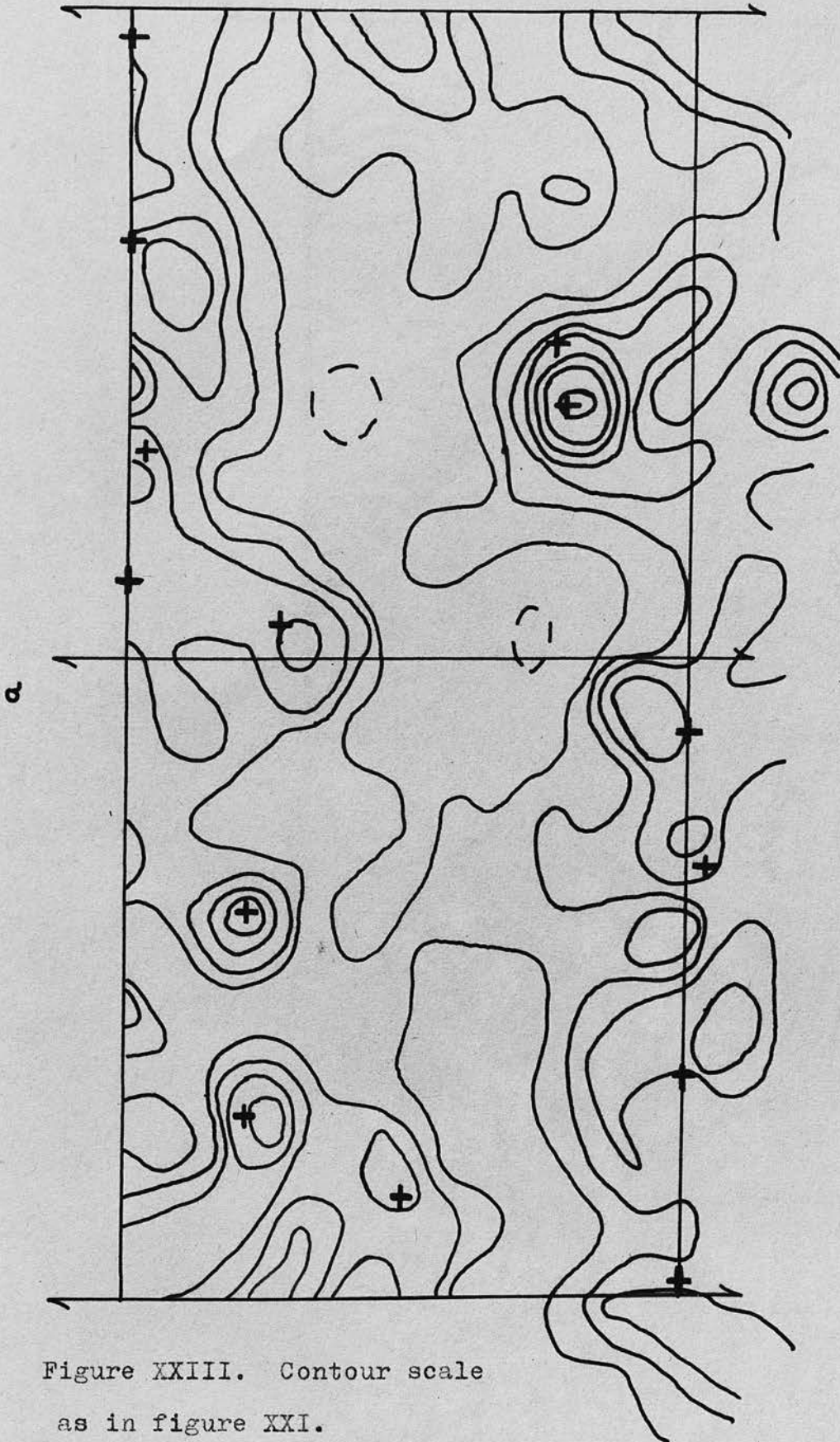


Figure XXIII. Contour scale
as in figure XXI.

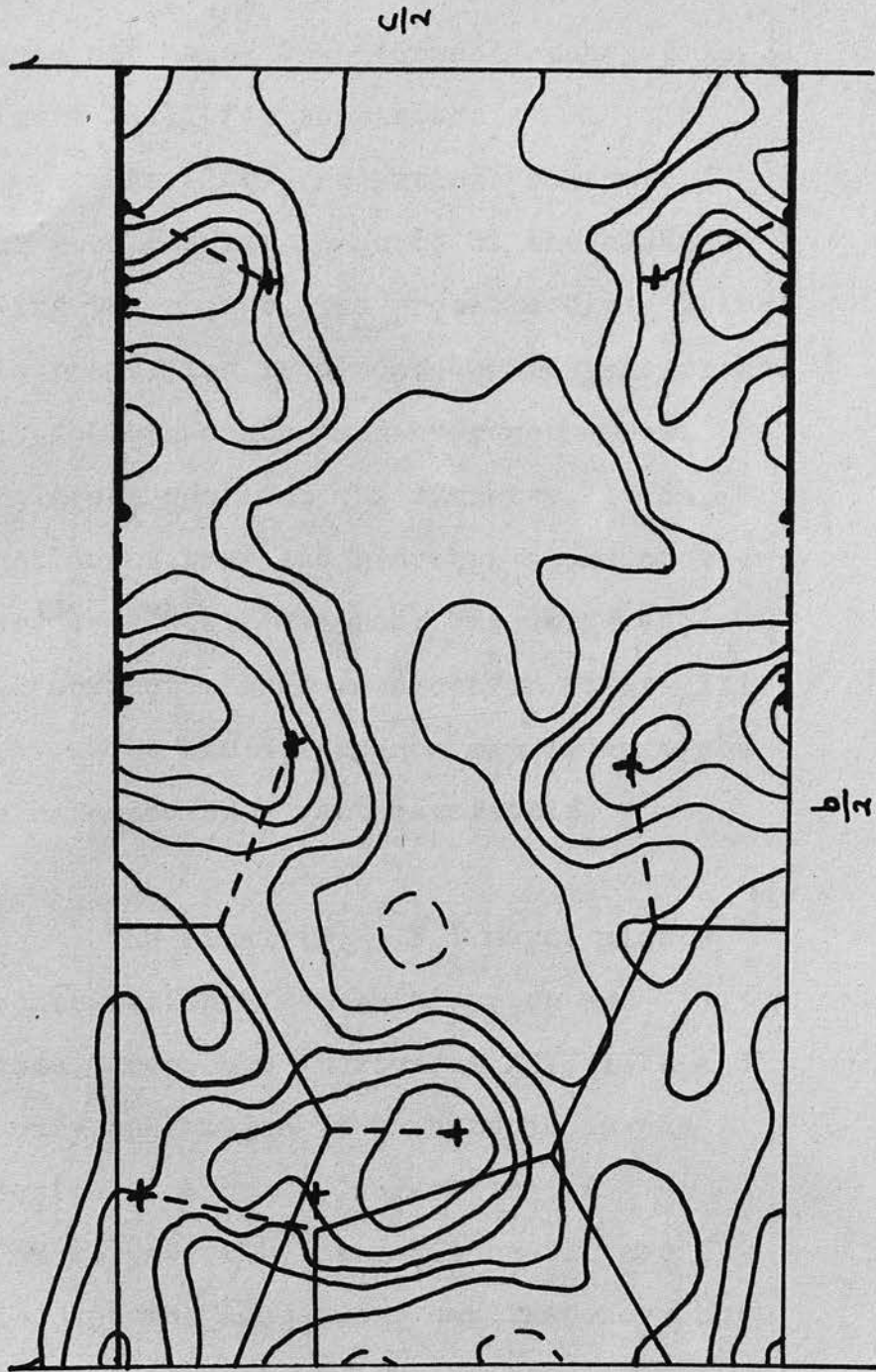


Figure XXIV. Contour scale as in figure XX.

The (010) projection of acenaphthene also gives poor hydrogen atom peaks under these conditions. The difference map using the "correct" phases, is shown in figure XXIII for comparison.

The (100) projection, however, gives rather good results in spite of the handicap of not knowing the phases. The probable explanation is that this projection is almost centrosymmetrical with respect to both carbon and hydrogen atoms, only the CH₂ group spoiling the symmetry. It is perhaps significant that the hydrogen atoms of the CH₂ group are least well defined. The difference map with the "correct" phases is shown in figure XXIV.

The hk0 difference map is as might normally be expected of a centrosymmetric projection.

The final ($F_o - F_c$) maps, with F_c including contributions from both carbon and hydrogen atoms, are shown in figures XXV, XXVI and XXVII. The only indication of a shift is in the (100) projection of atom C7, suggesting an alteration of z. The (010) projection does not confirm this, and the adjustment has therefore not been made. This shift had also been indicated in the penultimate cycle of refinement.

The value of the standard deviation of the electron density for the two non-centrosymmetric projections shows that discussion on the remaining electron density detail would not have

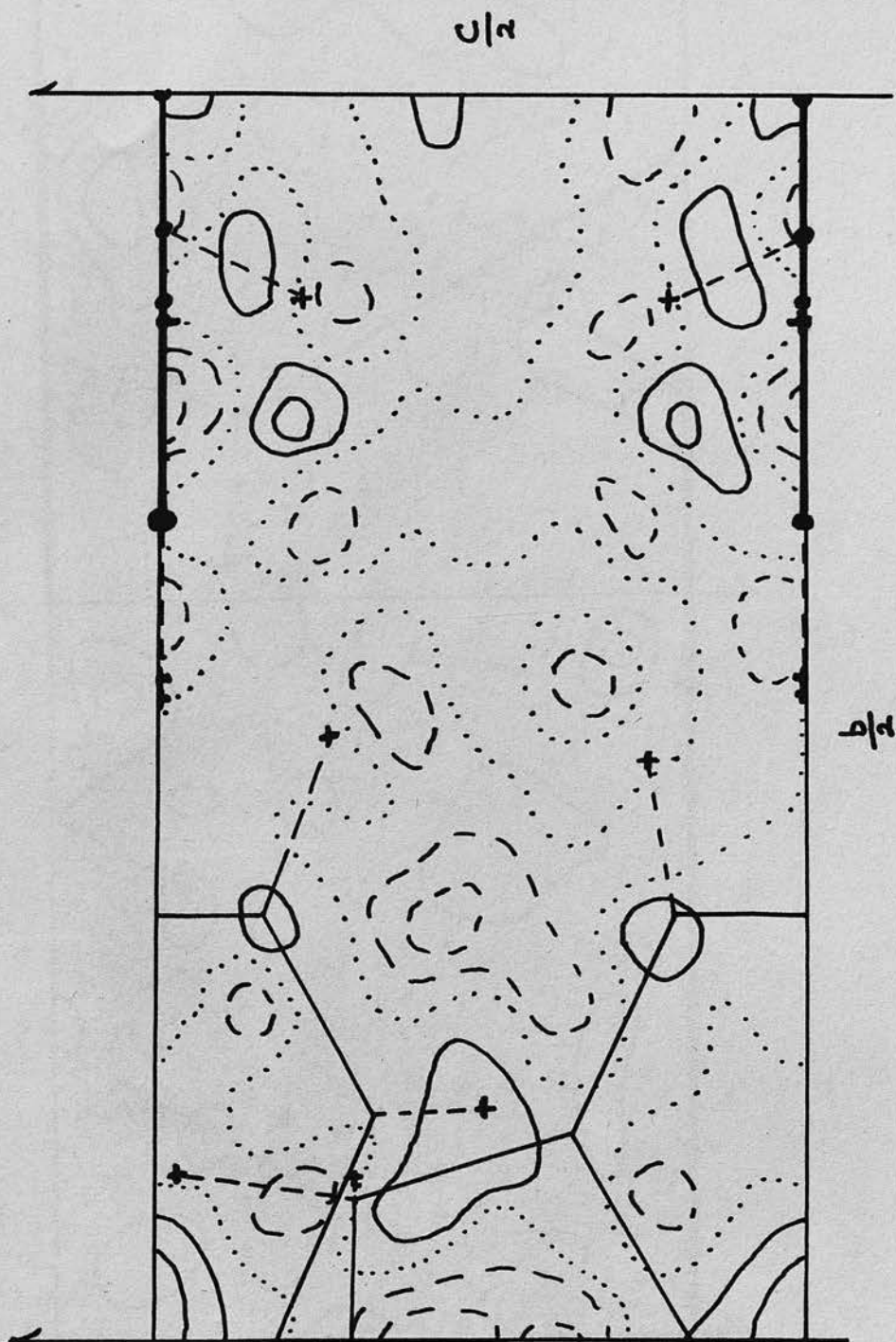


Figure XXV. The final $(F_o - F_c)$ synthesis for the (100) projection of acenaphthene. Contours every $0.2 \text{ e.}\text{\AA}^{-2}$, the negative contours being broken and the zero contour dotted.

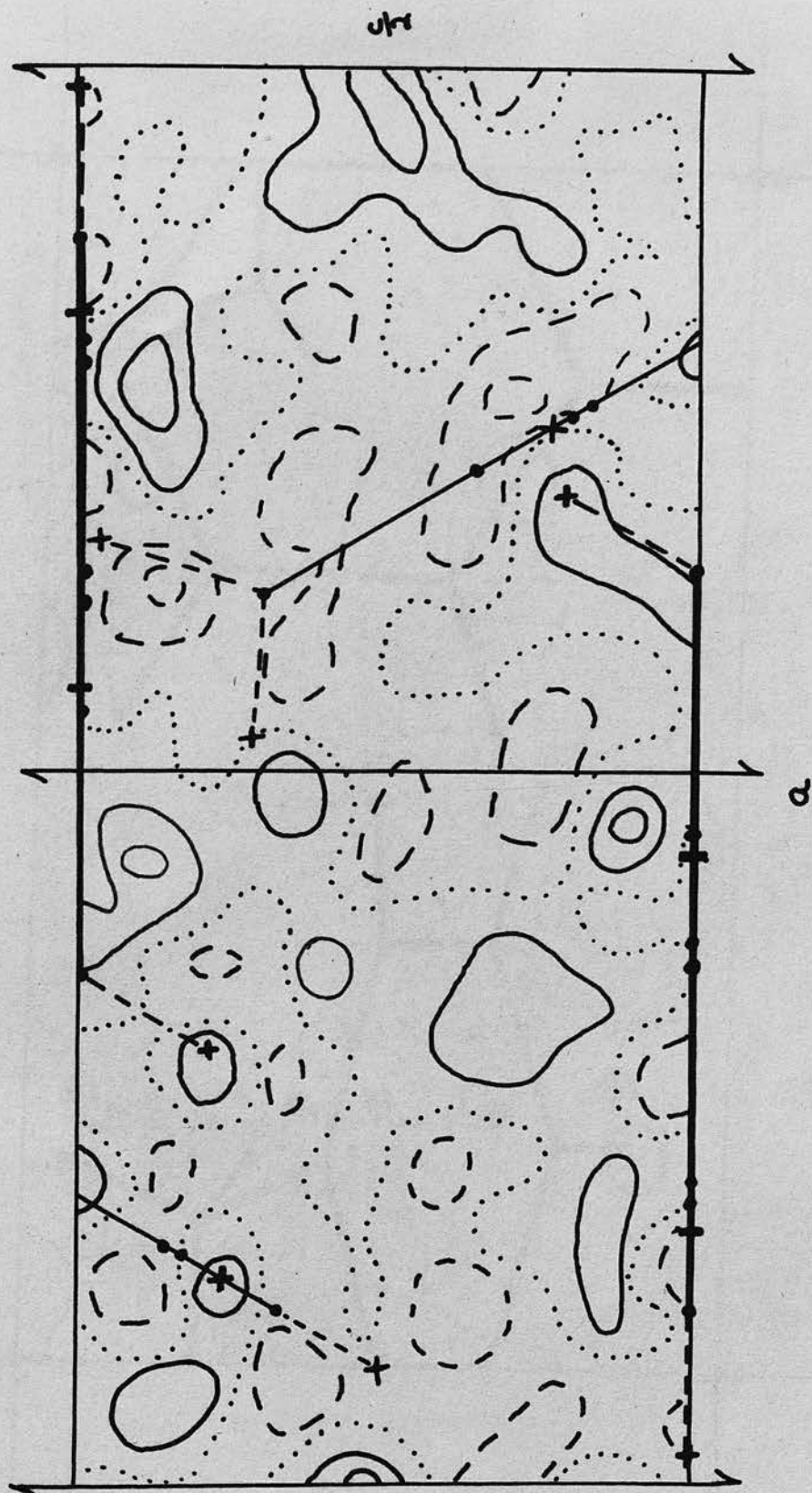


Figure XXVI. The final ($F_0 - F_0$) synthesis for the (010) projection of acenaphthene. Contour scale is twice that of figure XXV.

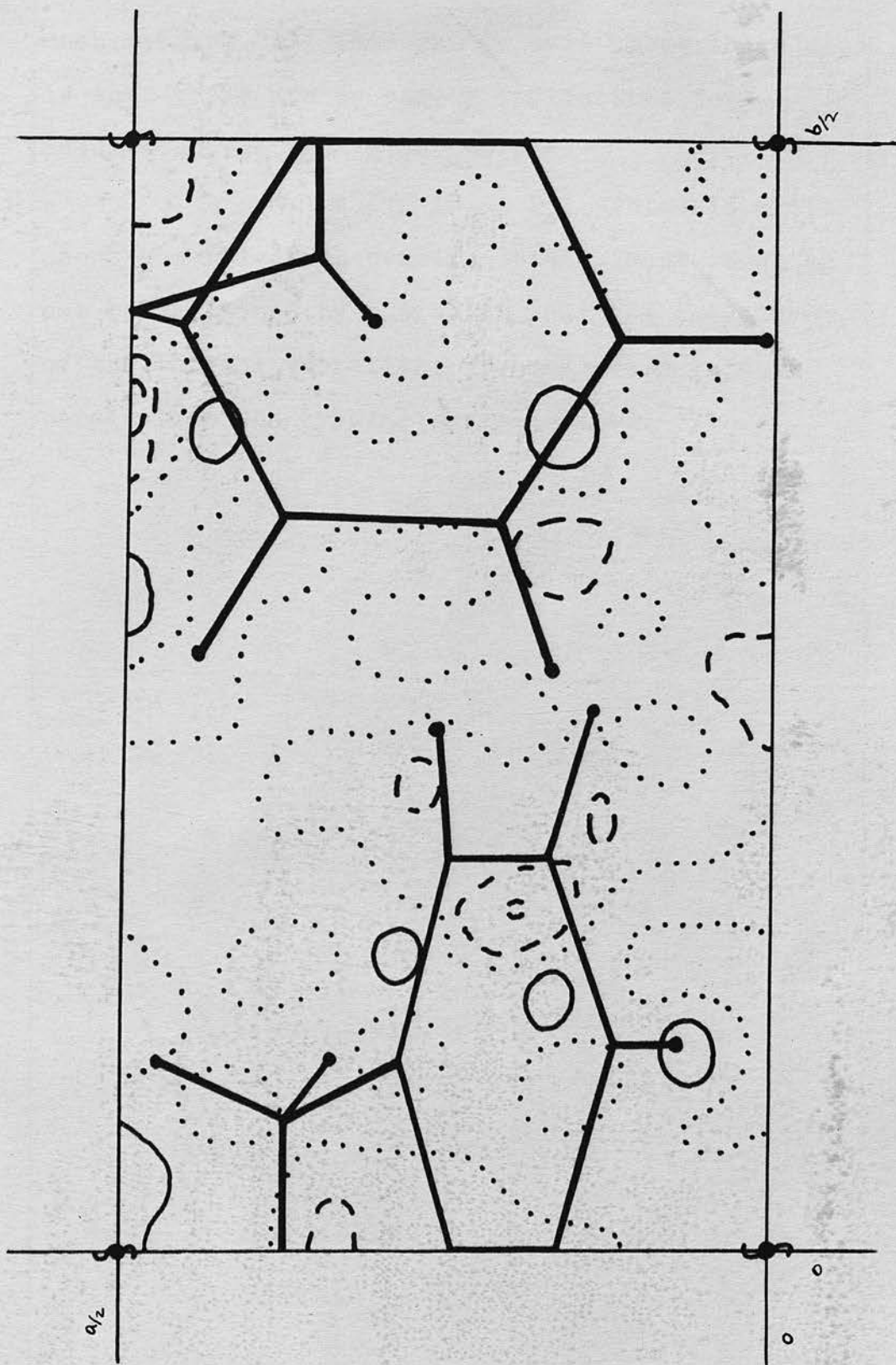


Figure XXVII. The final ($F_0 - F_c$) synthesis for the (001) projection of acenaphthene; contours as in figure XXV.

much meaning. All that can be said about these maps is that there are no strong indications for adjustments to atomic parameters.

The $hk0$ ($F_o - F_c$) synthesis still shows some electron density detail, most of which can be explained by admitting that the anisotropy of the thermal vibrations of some atoms is not parallel to the crystallographic axes.

DISCUSSION OF THE STRUCTURE.

Both the molecular and the crystal structures of acenaphthene are worth discussing in some detail.

The Molecular Structure.

Acenaphthene has a planar molecule, the hydrogen atoms fused directly onto the aromatic part of the molecule also lying in the same plane. As in the case of 2:13-Benzfluoranthene, the stress is again mainly in the angles, and none of the bond lengths are unreasonable. This time the analysis is accurate enough to give some meaning to a more detailed discussion of the observed bond lengths.

The C7-C7 bond length (1.540 Å) is now certainly not significantly different from 1.544 Å, the carbon-carbon distance in diamond. Hence, again there is no evidence of bond lengthening due to "mechanical" forces.

The C7-Cl bond length (1.524 Å) is somewhat shorter than a single bond, but not significantly so. It is also not significantly different from the C-CH₃ bond length in toluene, 1.51 Å (Keidel & Bauer, 1956). The shortening in the case of toluene is due to hyperconjugation, and there is a possibility of this phenomenon occurring in acenaphthene, since the arrangement

of the hydrogen atoms about C7 has the required symmetry. It is unfortunate that one cannot be certain that the bond shortening is real ($1.544 - 1.524 = 1.5\sigma$).

The bonds in the naphthalene nucleus do not differ significantly in length from those in naphthalene itself. The bond lengths in naphthalene (Cruickshank, 1957) are shown in figure XXVIII.

The C-H bond lengths this time also have some significance, since the coordinates of the hydrogen atoms were adjusted along with the carbon atom parameters, during the refinement. The C-H bond lengths are constant, within the limits of experimental error, and their weighted mean is 0.97 \AA , this value having a standard deviation of 0.05 \AA . This is somewhat longer than the average of those found in salicylic acid (Cochran, 1953), but not significantly so.

The bond angles have changed considerably. The Cl-C6-Cl bond angle has risen from 108° (required by the geometry of a regular pentagon) [or dropped from 120° (required by the sp^2 hybrid)] to 112° . Only two other angles have changed to any marked extent, namely Cl-C6-C5 and C6-C5-C4, and they too have changed by about 4° from 120° , the angle in a regular hexagon.

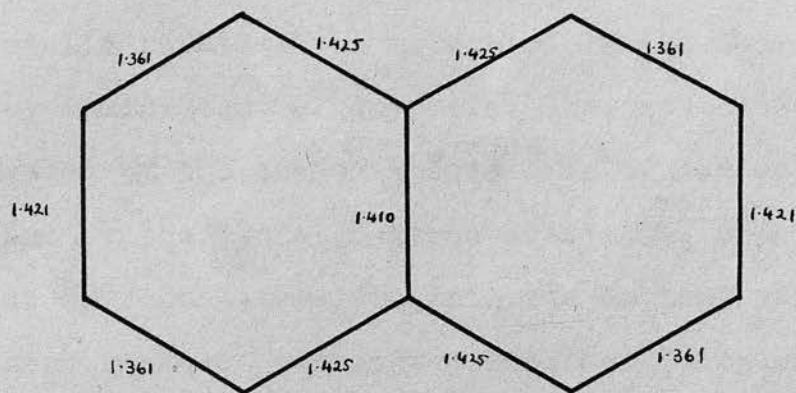


Figure XXVIII. The Bond Lengths in
Naphthalene.

The crystal structure.

The crystal structure of acenaphthene differs markedly in nature from those of other flat molecules. The molecules lie in two types of sheet, each about 7 Å thick; these sheets then pack alternately to give the three dimensional crystal.

Sheet A consists only of crystallographically A molecules, which pack in a way reminiscent of graphite. Some stability is provided by the second sheets B on either side of A, and by the hydrogen atoms of the CH₂ group; these hydrogen atoms fit into the hollows of the benzene rings of adjacent molecules. The packing of the molecules, with the distances between the centres of touching atoms, is shown in figure XXIX.

Sheet B has molecules packing in a way similar to that of other flat molecules, and the corresponding diagram is figure XXX.

These sheets fit onto one another so that the protuberances of one fit into the hollows of the other. The contacts between sheets are shown in figure XXXI.

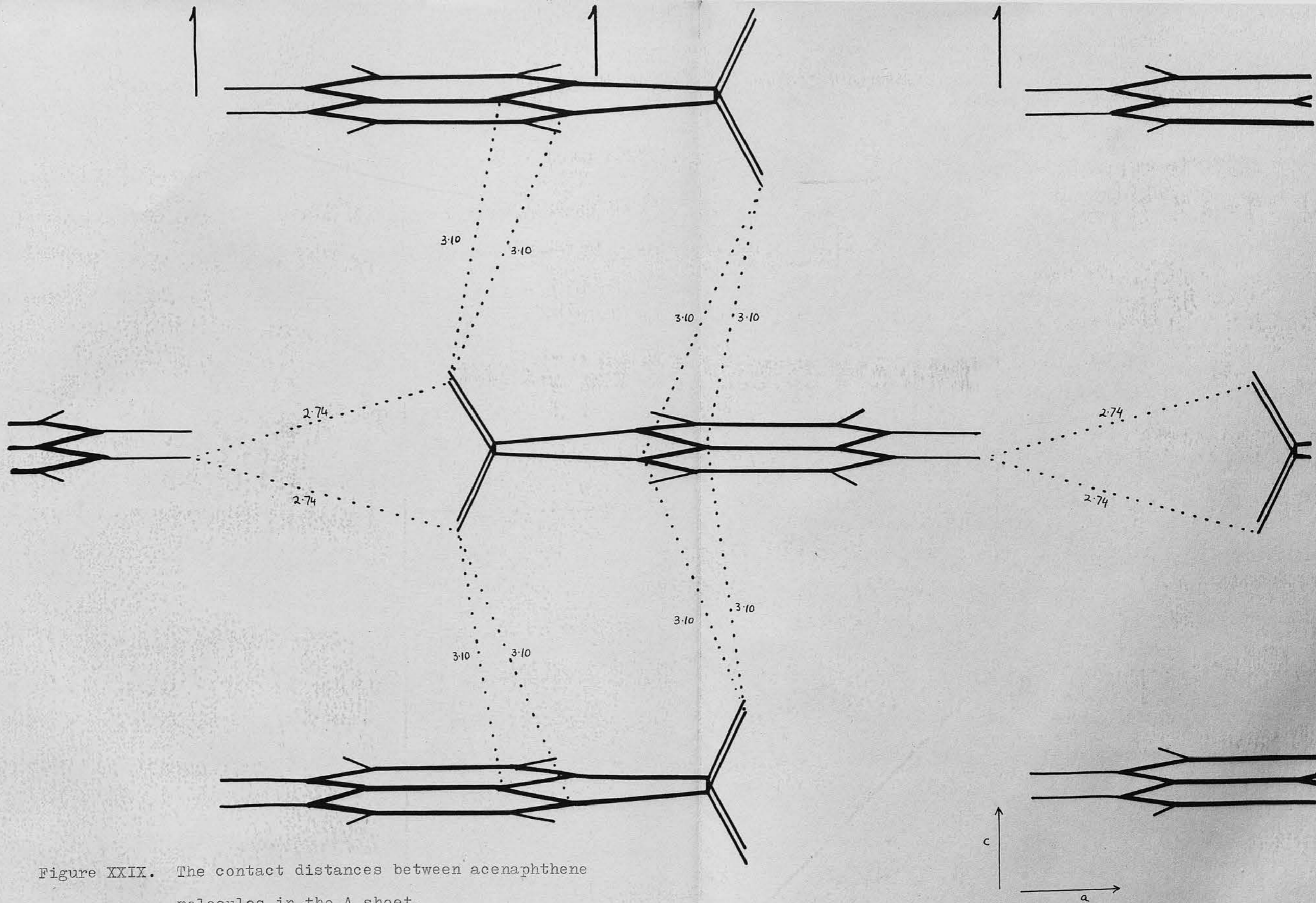


Figure XXIX. The contact distances between acenaphthene molecules in the A sheet.

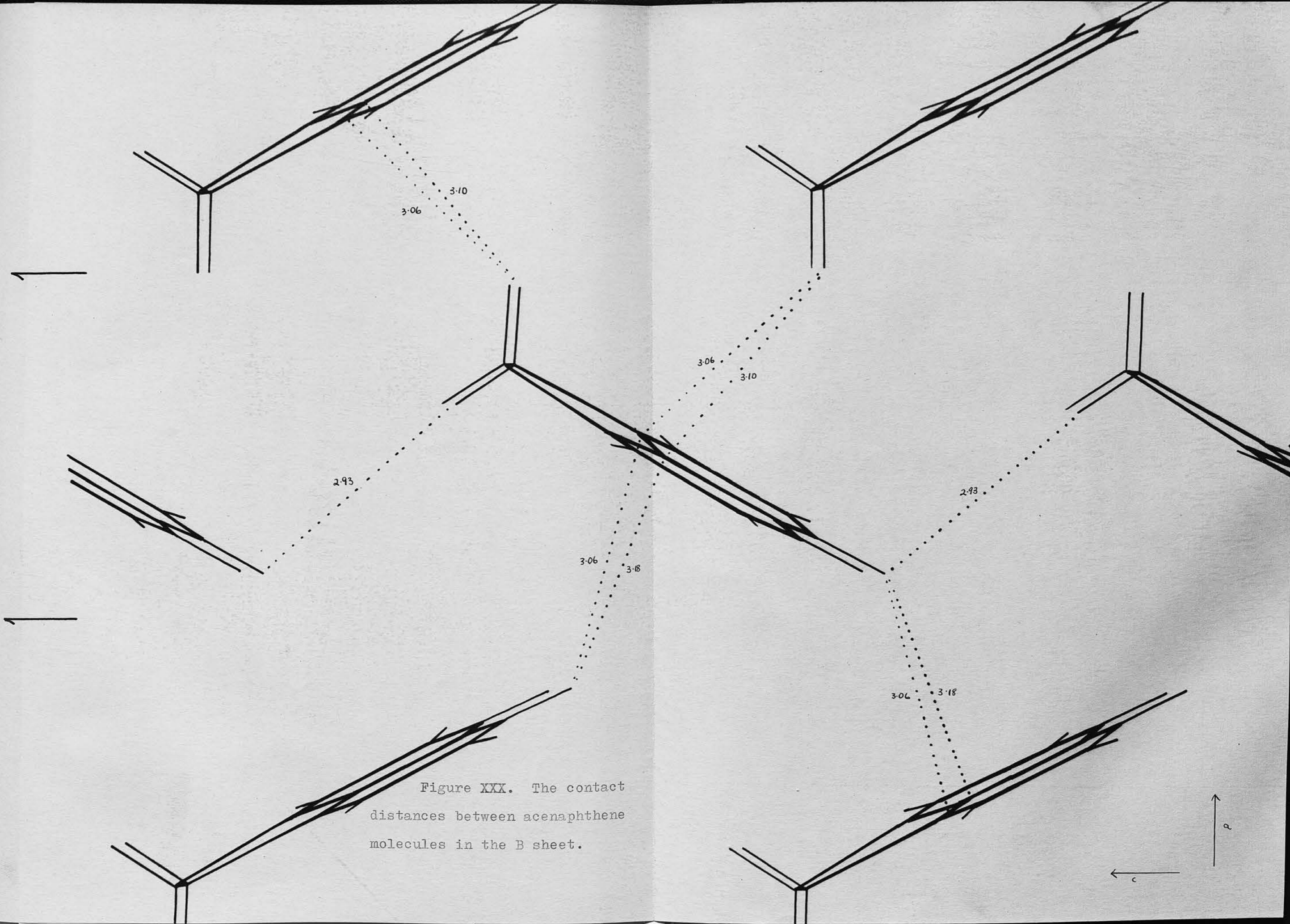


Figure XXX. The contact distances between acenaphthene molecules in the B sheet.

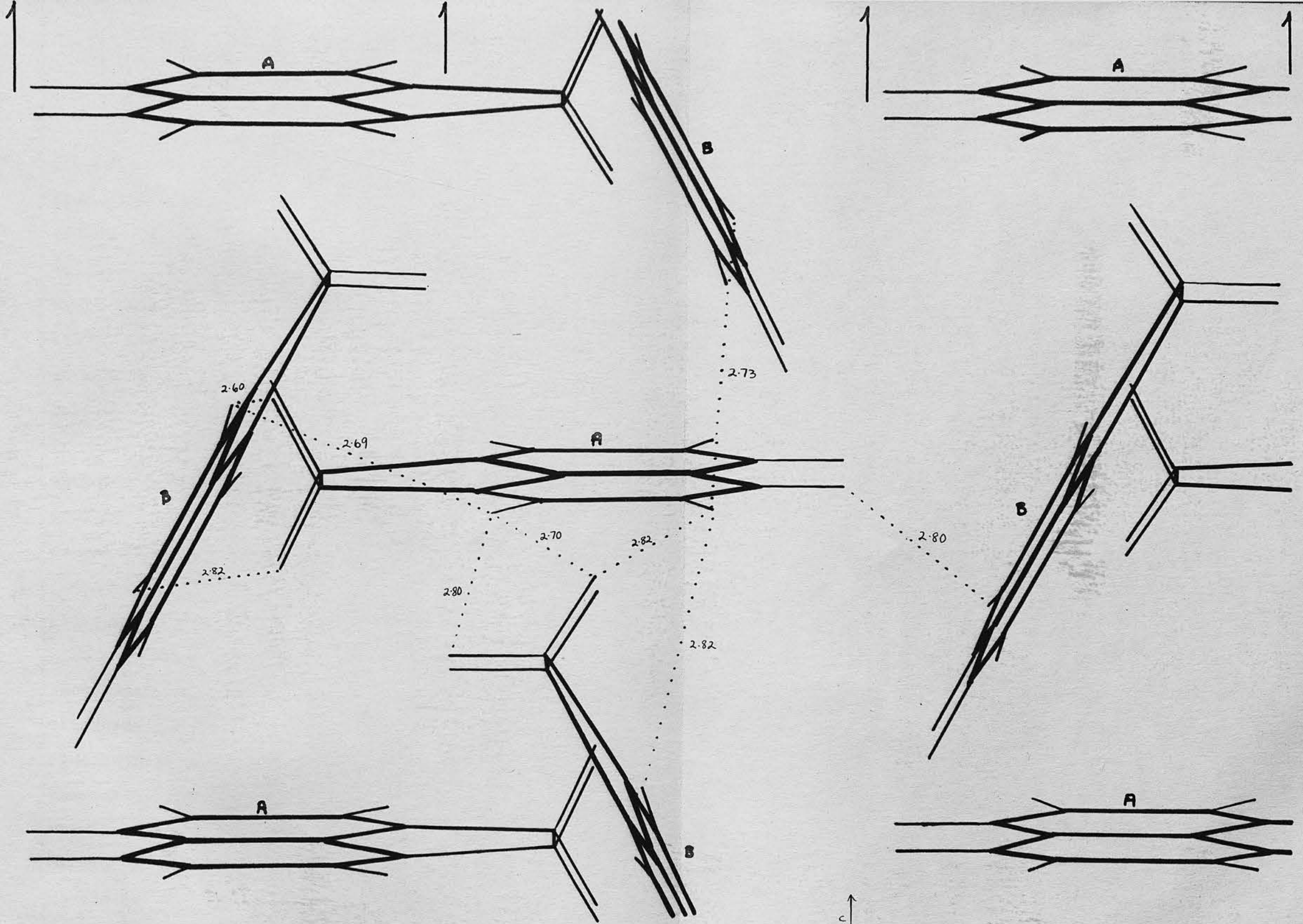
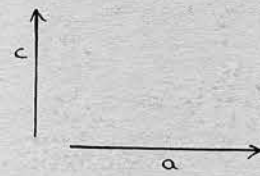


Figure XXXI. Contact distances between sheets A and B.



GENERAL DISCUSSION.

The study of the structures of crystals of aromatic hydrocarbons permits one to draw conclusions not only about the molecular dimensions and the variation of these from compound to compound, but also about the van der Waals radii of the atoms. In most substances the latter cannot be measured, since the packing is mainly determined by such effects as hydrogen bonding and coulomb attraction.

The two substances, whose structures have been discussed here, shed light both on the variation of molecular dimensions and on the packing of hydrocarbons.

Packing.

A study of aromatic hydrocarbons shows that they can be regarded as flat discs of thickness 3.42 \AA . The analysis of 2:13-Benz-fluoranthene gives the value 3.40 \AA , presumably because it was done at a low temperature. The van der Waals radius of a carbon atom, in a direction at right angles to the plane of the molecule, is, therefore, 1.71 \AA .

If this value is used for the carbon atoms in acenaphthene, one can calculate the hydrogen atom van der Waals radius from the C-H, as well as the H-H contact distances. In

acenaphthene there are 17 independent measurements which give 1.39 \AA as the average van der Waals radius. This agrees rather well with the average of the 7 measurements in anthracene, which is 1.36 \AA (Cruickshank, 1956). In acenaphthene the maximum deviation from this mean is 0.09 \AA , which is certainly not significant, and this suggests that the value 1.39 \AA is a constant of the hydrogen atom. In the very much more accurate analysis of anthracene the spread of values is rather larger, but the distances quoted are calculated from assumed positions of hydrogen atoms, and Cruickshank points out that the hydrogen atom coordinates obtained from the positions of the maxima of the peaks in the difference map, differ to quite an extent from these "theoretical" ones.

The results obtained from the acenaphthene analysis are very encouraging, and a similar set of calculations was carried out for 2:13-Benzfluoranthene. In view of what was said about anthracene, (and also because better results were obtained) the hydrogen atom x and z coordinates were altered as indicated by the difference map. Nothing could be done about the y coordinates, because the corresponding difference maps are of no help whatsoever, and the "theoretical" values were taken. The contact distances for 2:13-Benzfluoranthene are shown in figure XXXII, and are remarkably constant. The average hydrogen

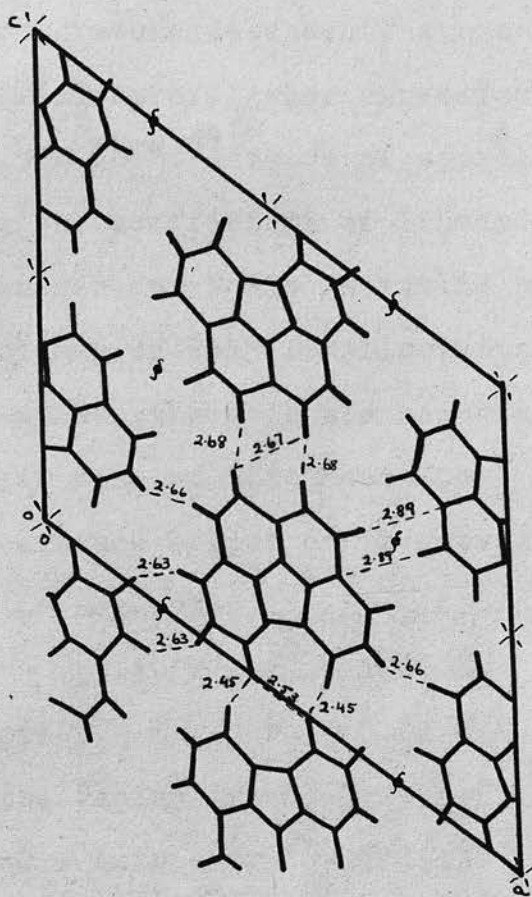


Figure XXXII. The intermolecular contact distances in the 2:13-Benzfluoranthene crystal.

atom van der Waals radius is 1.29 \AA , and the decrease in this value, although not significant, is perhaps partly due to the effect of temperature.

A covalent bond length must be slightly temperature dependent, since diamond does have a coefficient of linear expansion, whose value is 0.9×10^{-6} . A means of approximately determining the coefficient of linear expansion of the hydrogen van der Waals radius is by considering the cell volumes of 2:13-Benzfluoranthene at the two temperatures, the molecule being approximated to a circular disc of thickness 3.4 \AA and radius r (the temperature effect on the covalent bond length may be neglected).

$$\text{At } -97^{\circ}\text{C} \quad 3.40 \times 4\pi r^2 = 1086 \text{ \AA}^3$$

$$\text{and therefore} \quad r = 5.04 \text{ \AA}$$

$$\text{At } +23^{\circ}\text{C} \text{ the radius is} \quad r + \delta r$$

$$\text{and} \quad 3.42 \times 4\pi (r + \delta r)^2 = 1115 \text{ \AA}^3$$

$$\text{Hence} \quad \delta r = 0.05 \text{ \AA}$$

giving a coefficient of linear expansion of 3×10^{-4} . Similar calculations for naphthalene, whose coefficient of linear expansion is 1.07×10^{-4} give the same answer.

If the angle between the molecular plane and the (010) plane in the 2:13-Benzfluoranthene crystal is the same at the two temperatures (which is not necessarily so), then the coefficient of linear expansion of the carbon atom van der Waals radius is 5×10^{-5} . The

magnitude of the expansions of the a and c axes does not allow the angle to become any smaller with rise in temperature, and hence 5×10^{-5} is an upper limit.

The study, therefore, of the packing of acenaphthene and 2:13-Benzfluoranthene leads to the conclusions that the distances between the centres of touching atoms are constant for the atoms involved in the contact, and that the van der Waals radius of a hydrogen atom is 1.4 \AA , and the semithickness of an aromatic molecule is 1.71 \AA , at room temperature, the corresponding coefficients of linear expansion being of the order of 3×10^{-4} and 5×10^{-5} respectively, in comparison with 1×10^{-6} for C-C covalent bonds. Thus the thermal expansion of a molecular compound is primarily determined by the temperature effect on the van der Waals distances.

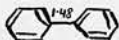
Molecular Dimensions.

The crystal structures of acenaphthene and 2:13-Benzfluoranthene were examined to study what form the stress will take in these strained molecules.

Only the analysis of acenaphthene is accurate enough to warrant any discussion on changes in bond length, and the results from 2:13-Benzfluoranthene can only be used to confirm

any conclusions that may be drawn.

As has already been said, all the aromatic bonds in acenaphthene have lengths which are not significantly different from those in naphthalene, and the aliphatic single bond, C7-C7, is almost exactly the same length as the C-C bond in diamond. In the more strained molecule of 2:13-Benzfluoranthene the bond C₁₄ - C₁₅ is 1.49 Å long, which again is not long. In none of the Kekulé structures for this molecule is this bond a double bond, and the observed length is in remarkable agreement with similar bonds in other substances, namely diphenyl (Dhar, 1932)



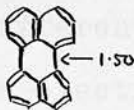
p-diphenyl benzene (Pickett, 1933)



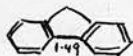
benzoquinone (Robertson, 1935a)



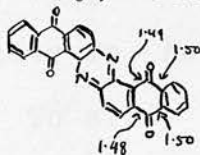
perylene (Donaldson & Robertson, 1953a)



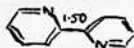
fluorene (Burns & Iball, 1954)



indanthrone (Bailey, 1955)



and 2:2'-bipyridine (Merritt & Schroeder, 1956)



All these substances are completely aromatic, but the labelled linkages can never be double bonds in any of the Kekulé structures. Thus the length of an "aromatic single" bond is about 1.49 Å. The bond C₁₄-C₁₅ in 2:13-Benzfluoranthene is expected to be under a very large strain, and yet there is no suggestion that its length has increased. There is, therefore, no evidence whatsoever for bond lengthening due to "mechanical" forces, and very high accuracy would be required in X-ray analysis to detect any changes, if they do exist. Charge effects, such as occur in acenaphthylene, where the double bond will conjugate with the naphthalene nucleus, will, of course, be expected to affect bond lengths.

There is no deviation from planarity in either of the two molecules, and so the carbon atoms have their valency electrons in the sp² hybridised state, with the exception, of course, of C7 in acenaphthene. But some of the bond angles are significantly different from 120° in both molecules. Hence the electrons either exist in orbitals which are coplanar but not at 120° to one another, or, if the angles do also remain constant, the electrons take part in "curved" bonds. The latter possibility is, however, unlikely.

To study the effects of mechanical strain in an aromatic molecule only the changes in angles need be considered (in non-planar molecules the immediate environment of each atom is not very

far from coplanarity). A comparison of the molecular shapes of acenaphthene, fluorene and 2:13-Benzfluoranthene bears this out, see figure XXXVIII in which the aliphatic bonds are dotted to distinguish them from the aromatic ones.

A good representation of a molecule can be obtained by constructing a model from "carbon atoms" joined by non-elastic bonds between which are placed elastic wedges, thus



so that, unless there is some mechanical disturbing force, the bonds will be at 120° to one another.

The carbon - hydrogen bond lengths are only of interest in so far as that they have actually been measured. The average in acenaphthene is 0.97 \AA , and, using the observed hydrogen atom positions, the average bond length in 2:13-Benzfluoranthene is 1.02 \AA , individual values varying from 0.88 to 1.14 \AA . All that can be said about the second average is that it is encouraging that it does not conflict with the acenaphthene one.

While, in this discussion, the 2:13-Benzfluoranthene determination has been used only as confirmation for any conclusions drawn from the acenaphthene structure, it must not be

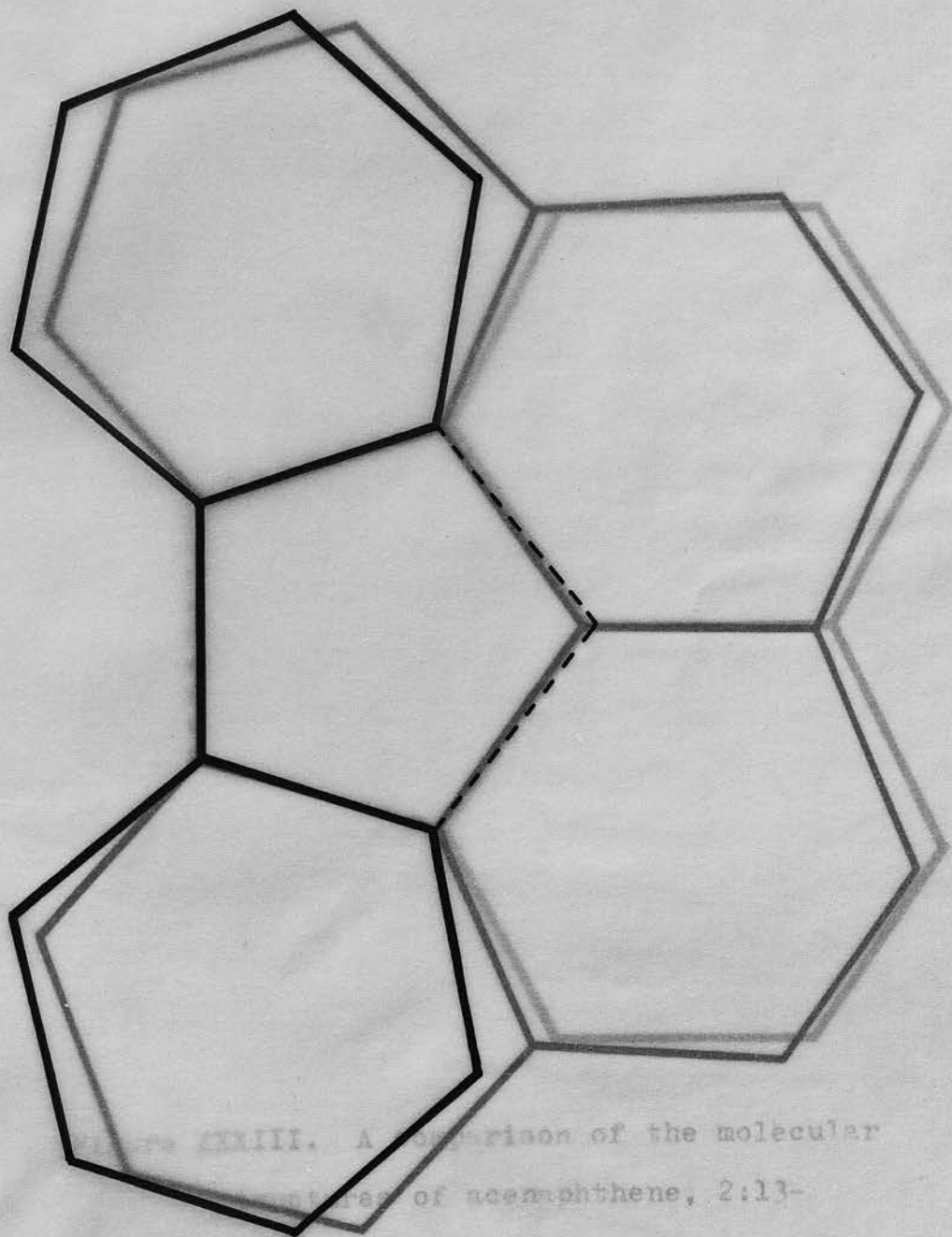


Figure XXXIII. A comparison of the molecular structures of acenaphthene, 2:13-dimethylfluoranthene and fluorene.

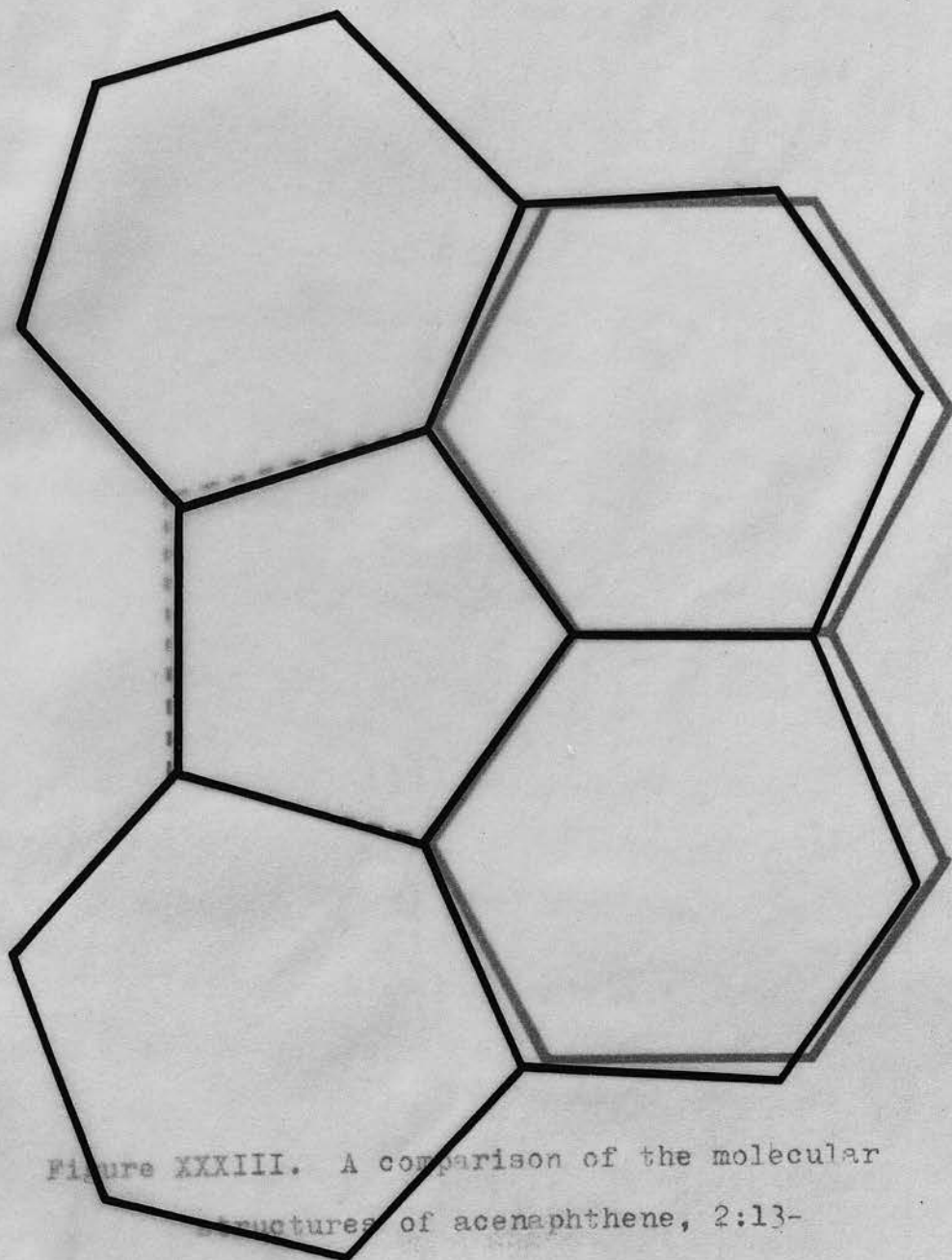


Figure XXXIII. A comparison of the molecular
structures of acenaphthene, 2:13-
Benzfluoranthene and fluorene.

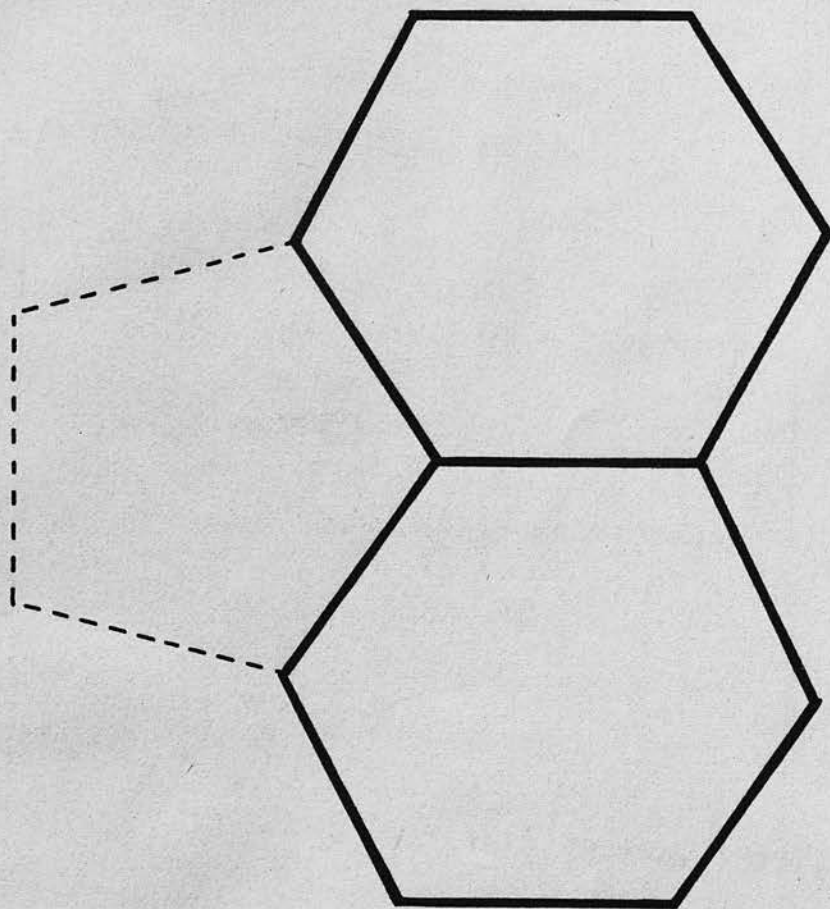
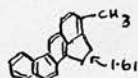
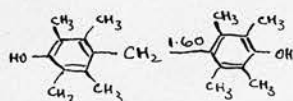


Figure XXXIII. A comparison of the molecular structures of acenaphthene, 2:13-Benzfluoranthene and fluorene.

regarded as an inaccurate analysis. It suffers by comparison with the acenaphthene analysis, but the determination is of sufficient precision to reveal any large distortions which might be expected in such a highly strained molecule. This analysis alone would have sufficed to show that bond length distortions are very small, were it not for the contradictory evidence of some other studies, e.g. on acenaphthene, 20-methylcholanthrene (Iball & MacDonald, 1955),



bis-hydroxy-duryl methane (Chaudhuri & Hargreaves, 1956),



and symmetrical 1:2:3:4-tetraphenyl-cyclobutane (Dunitz, 1949)



However, the analysis of di-p-xylylene (Brown, 1953), a very strained molecule,



supports the findings of the 2:13-Benzfluoranthene research. It is suspected that, except perhaps for the work on 1:2:3:4-tetraphenylcyclobutane and di-p-xylylene, these investigations were not of adequate precision to warrant any serious consideration. The re-examination of acenaphthene

showed that the previous work did lack precision, and the present study is one of considerable accuracy. The results, supporting the findings of the 2:13-Benzfluoranthene work, must carry some weight in any discussion on strained molecules.

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