

ELECTRON DENSITY MAP OF ANTHRAQUINONE CRYSTAL

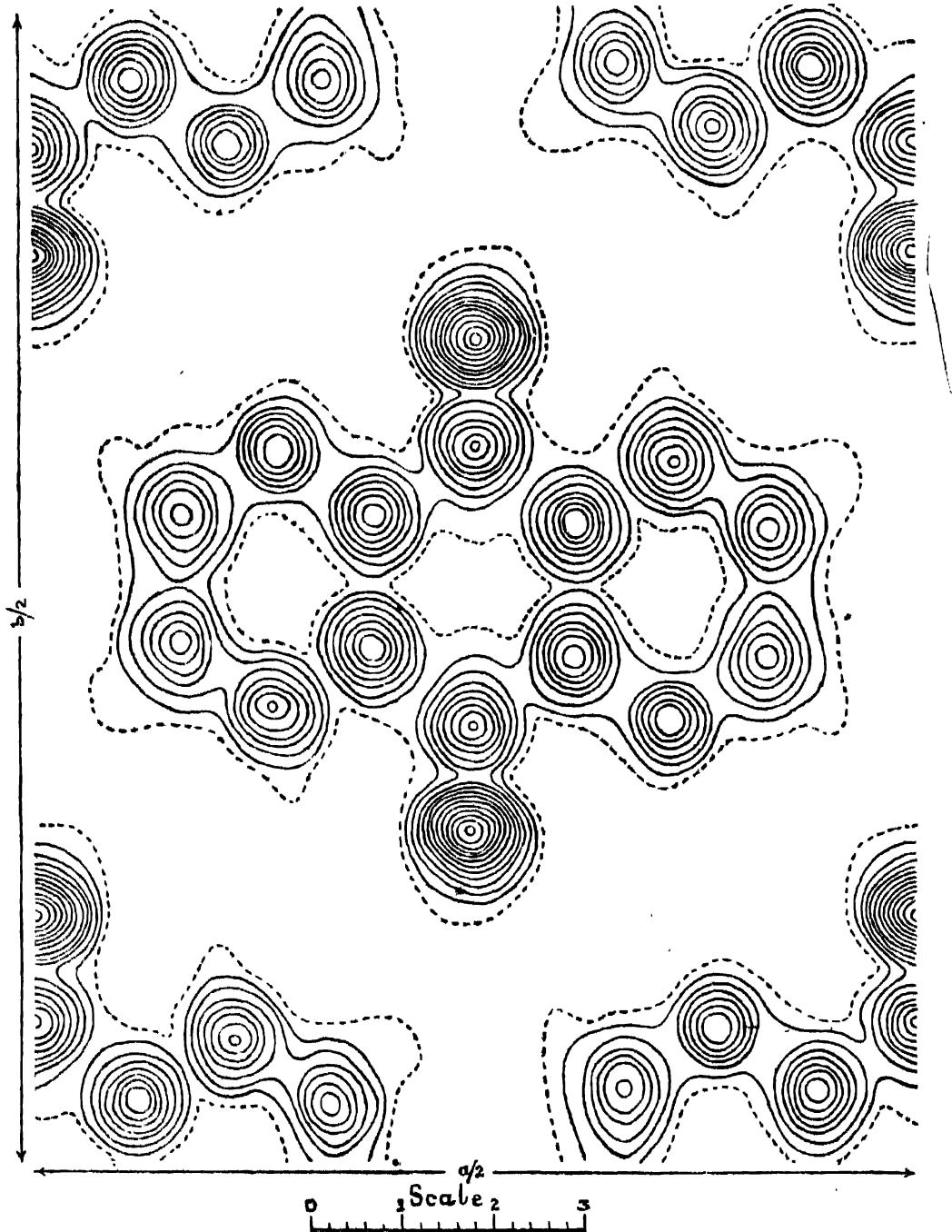
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ABSTRACT. It was shown by the author (Sen, 1940) that anthraquinone really belongs to the monoclinic class and not to the orthorhombic class as was assumed to be previously. A revised projection of electron density on the (001) plane of anthraquinone crystal by the two-dimensional Fourier analysis method has been carried out in the light of the new space group derived after re-classification of the crystal into monoclinic system. Much larger number of reflecting planes have been taken into account in the present analysis to make the Fourier series more convergent. Co-ordinates of atomic centres in the projection have been obtained with greater accuracy. Fresh calculation of structure factors have shown much better agreement with the observed values. Observed difference in intensities of h_0k_00 and $h_0\bar{k}_00$ reflections (referred to orthorhombic ones), which are not possible for an orthorhombic crystal, are found to be of real significance in the light of the present analysis.

In an earlier communication, it was shown by the author (Sen, 1940) that anthraquinone really crystallises in the monoclinic class having a space group $C_{2h}^2P2_1/a$. Previously the crystal had been assumed to be orthorhombic. Banerjee and Sen (1938) had obtained a projection of electron density on the (001) plane of anthraquinone crystal by the two-dimensional Fourier analysis method, but in that analysis the crystal was assumed to be orthorhombic in accordance with the space group as determined by the previous workers. But when it was found that the anthraquinone crystal was really monoclinic with $C_{2h}^2P2_1/a$ as its space group, it was primarily important to revise the electron density projection on (001) plane obtained on the basis of the orthorhombic hypothesis in the light of the new space-group of the crystal. The origin of pseudo-symmetries observed in the planes of reflection in the older orthorhombic system will be readily found by transforming the older indices $h_0k_0l_0$ into their corresponding indices in the monoclinic system. It can easily be shown that a plane $h_0k_0l_0$ on the older orthorhombic nomenclature corresponds to $h_mk_ml_m$ in the new monoclinic system, where $h_m = (h_0 + k_0)/2$, $k_m = l_0$ and $l_m = (h_0 - k_0)/4$. For h_0k_00 planes it was found that (i) $h_0 + k_0$ is divisible by 4 which means h_m is divisible by 2, (ii) $h_0 - k_0$ is divisible by 4 means that l_m may have any value for h_m0l_m planes. Also for $00l_0$ planes, l_0 is found to be even, i.e., in $0k_m0$ planes, k_m is even. These are in fact the criteria for space group $C_{2h}^2P2_1/a$. The pseudo-symmetries in the orthorhombic cell actually appeared for taking a bigger unit cell (orthorhombic) while the real fundamental cell (monoclinic) in the crystal is much smaller.

For obtaining the electron density map projected along the symmetry axis we may retain the pseudo-orthorhombic system of co-ordinates because this direction happens to be a crystallographic axis in both the systems and the other two pseudo-orthorhombic axes are the diagonals of the fundamental

monoclinic lattice which may be approximately regarded for the purpose of the Fourier summation to be mutually perpendicular, the actual angle between them as calculated from the measured dimensions of the cell being $90^{\circ}42'$. There is, however, a fundamental difference between the summations carried out on

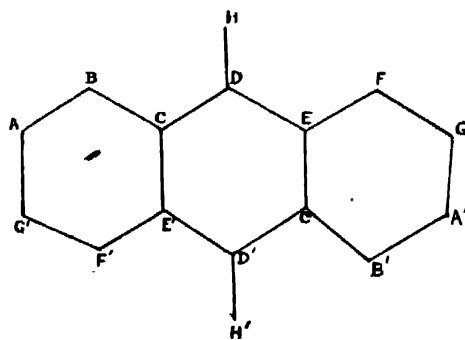


Projection along the c -axis. The dotted line represents the one electron line, the other lines are drawn at intervals of one electron per \AA^2 .

FIG. 1

the assumption of an orthorhombic cell and those according to the correct monoclinic cell. That is due to the difference in the structure factors of h_0k_00 and $h_0\bar{k}_00$ planes. In evaluating electron density on the symmetry plane, the mean of structure factors for h_0k_00 and $h_0\bar{k}_00$ planes were taken on the basis of the earlier assumption of orthorhombic lattice. The actual differences observed in the intensity measurements of those planes were then believed to be spurious or due to experimental errors and hence the mean of the two values were used for both h_0k_00 and $h_0\bar{k}_00$ planes in the Fourier summation. The observed difference in the intensities of h_0k_00 and $h_0\bar{k}_00$ reflections were later found to be of real significance as the h_mk_m0 and $h_m\bar{k}_m0$ planes when transformed to the new monoclinic system represent different planes altogether, reflections from which cannot be expected to be of the same intensities. So the contributions of the h_mk_m0 and $h_m\bar{k}_m0$ planes towards Fourier summation were worked out separately on the basis of their respective intensity measurements. Further, a highly overexposed Weissenberg photograph was taken round the old c -axis in order to take the weaker reflections also into account and thereby make the Fourier series more convergent. Structure factors of 92 planes have been used in the present Fourier summation while those of only 44 planes were used in the previous summation to obtain the electron density map published before.

The Fourier summation was carried out over a half of one molecule which forms the asymmetric unit of structure, the axial subdivisions being $a_0/48$ and $b_0/48$. But for accurate location of the atomic centres, additional summations were carried out at closer intervals with axial subdivisions $a_0/96$ and $b_0/96$ round about the atomic centres. The electron density distribution thus obtained is shown in Fig. 1. The x and y co-ordinates finally obtained are given in Table I for which the key to the symbols for the atoms will be obtained from the structural formula given in Fig. 2.



Structural formula of anthraquinone. ABCDEFG A'B'C'D'E'F'G' are carbon atoms and H and H' are oxygen atoms. H-atoms are not shown.

FIG. 2

TABLE I

Co-ordinates of Atoms referred to Orthorhombic cell
Molecular centre of symmetry at (000) as origin

Atom	x (in A.U.)	(in A.U.)
A (CH)	- 3.253	0.765
B (CH)	- 2.198	1.447
C (C)	- 1.115	0.745
D (C)	0.038	1.476
E (C)	1.164	0.649
F (CH)	2.236	1.311
G (CH)	3.308	0.615
H (O)	0.049	2.623

Fresh calculation of structure factors of all $h,k,0$ planes were made with the final x and y co-ordinates of atoms obtained from the electron map. The agreement between the measured and calculated values of structure factors is considerably better as compared to those worked out with the structure obtained previously. The differences in the measured structure factors of certain pairs of hko and $h\bar{k}o$ planes (arising from the observed differences in the intensities of their reflections) were found to be in very good agreement with the calculated values of structure factors obtained from the final structure. It is, therefore, worth noting that the final structure, owing to its slight deviation from the orthorhombic symmetries, have accounted for the observed differences of intensities between pairs of hko and $h\bar{k}o$ planes, which previously was thought to be spurious.

In conclusion I wish to express my sincere thanks to Prof. S. N. Bose for his keen interest in this work and to Prof. K. Banerjee for suggesting the problem and advice during the progress of the work.

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REFERENCES

- Banerjee, K. and Sen, S. N. (1938), *Science and Culture*, 3, 570.
Sen, S. N. (1940), *Science and Culture*, 8, 717