(siehe (41)). Für das weniger absorbierte Wellenfeld No. 2 gibt die Differenz der Geraden und der vierten Kurve den Absorptionskoeffizienten; man erkennt, wie gering dieser in der Gegend von $\beta_r = \frac{1}{2}E$ ist. Die Einheit $E$, in welcher die Figur $\beta_r$ misst, beträgt $2{,}0 \times 10^{-5}$. Dieselbe Einheit gilt auch für Fig. 2(*a*), welche für $D = 1 \times 10^{-2}$ cm. in Kurve I die rechte Seite von (37), in Kurve II die rechte Seite von (38) angibt, beide ohne das Cosinusglied. Die Amplitude des Cosinus, $\frac{1}{2}\mathfrak{Cos}^2 v_r$, gibt Kurve III; man erkennt, dass eine Berücksichtigung dieses dritten Gliedes an dem Verlauf der Figuren I und II qualitativ nichts änderte. Dass Kurve I und II sich genau im Punkt $\beta_r = 0$ schneiden, ist wegen $|\chi_{\bar{h}}| = |\chi_h|$ eine strenge Folgerung aus (37) und (38) und findet sich auch in den folgenden Figuren.

Fig. 2(*b*) und 2(*c*) sind unter der Voraussetzung berechnet, dass die Kristallschicht von zwei Würfelflächen 010 begrenzt wird. In Fig. 2(*b*) ist die Schichtdicke $D$ zu $1 \times 10^{-2}$ cm., in Fig. 2(*c*) zu $2 \times 10^{-2}$ cm. angenommen. Die Kurven I, II und III haben dieselbe Bedeutung wie in Fig. 2(*a*). Ähneln sich die Figuren 2(*a*) und 2(*b*) weitgehend, so ist in Fig. 2(*c*) das Maximum viel stärker ausgeprägt und etwas näher bei $\beta_r = 0$. Die Einheit $E$ für $\beta_r$ ist in diesen Figuren $2{,}45 \times 10^{-5}$.

Zwar dürfen wir diese Kurven wegen der Willkür der Gleichung (18) nicht als quantitatives Abbild der Wirklichkeit nehmen und müssen für einen Vergleich mit der Erfahrung auch noch berücksichtigen, dass sie für den anderen, im Experiment nicht abgetrennten Polarisationszustand (die elektrische Schwingung *in* der Ebene beider Strahlen) etwas flauer verlaufen. Aber sie stimmen doch qualitativ zu den erwähnten Beobachtungen Borrmann's und geben Grund zu der Hoffnung, dass weitere Untersuchung über die Absorption der Röntgenstrahlen volle Übereinstimmung zwischen Theorie und Erfahrung ergeben wird.

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*Acta Cryst.* (1949). **2**, 113

# A Punched-Card Modification of the Beevers-Lipson Method of Fourier Synthesis

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(*Received* 5 *November* 1948)

A description is given of a punched-card system for Fourier synthesis which may be regarded as a mechanized version of the original Beevers-Lipson method, and which has been used successfully for the evaluation of two- and three-dimensional Fourier series.

## Introduction

In X-ray crystal-structure analysis the calculation of electron-density distributions by Fourier synthesis is a frequently occurring task, for which the methods of Robertson (1936) and of Lipson & Beevers (1936) have been widely employed. Methods making use of a punched-card system have been described by a number of investigators (Shaffer, Schomaker & Pauling, 1946; Comrie and others (unpublished); Cox, Gross & Jeffrey, 1947). The method used by the American workers is elaborate and requires equipment not available in this country, while that used in connexion with work on penicillin was on such a scale that it could be carried out only by a professional computing service. Cox and his collaborators have developed a method which can be operated by people not specially trained in the use of Hollerith equipment. It is not considered suitable for the evaluation of the electron density at points throughout the unit cell, but is used to explore the electron density over limited regions by means of sectional syntheses. The present scheme is based on the latter method, but is modified so as to resemble more closely the original method of Lipson & Beevers, of which it may be regarded as a mechanized and extended version.

It employs a minimum of Hollerith equipment, namely, a standard E 6/6 tabulator. We were able to make use of Hollerith equipment installed in the University Mathematical Laboratory and kindly provided by the British Tabulating Machine Co. Ltd.

### Details of equipment

The punched cards were prepared from a master pack kindly provided by Prof. Cox. This consisted of cards carrying the functions

$$A^{\cos}_{\sin} n \,.\, 2m3^\circ \quad \text{and} \quad A^{\cos}_{\sin} n \,.\, (2m-1)\,3^\circ,$$

$$\text{for} \quad A = \pm 1,\ \pm 10,\ \pm 100; \quad n = 0, 1, \ldots, 20;$$

$$\text{and} \quad m = 1, 2, \ldots, 15.$$

The information is recorded in the form of rectangular holes representing, by their vertical positions on the card, the numbers 0 to 9. A complete description of the arrangement of the data on the cards is given in the paper by Cox *et al.* (1947); only such of it as is relevant to the present discussion will be given here. The eighty card columns were divided into sixteen groups, or fields, of five columns each. The first five columns were used to give descriptive information (amplitude, wave number, etc.), while values of the function for fifteen values of $m$ were recorded in the remaining fifteen additive fields. The eight cards for a given $A$ and $n$, corresponding to positive and negative amplitudes, cosine and sine functions, and odd and even series of 6° intervals, were distinguished by over-punching. Of the five columns in each field four were used to give positive values of the function to two decimal places, and five for giving negative values as complements with respect to 999·99. These cards have been used to prepare a new master pack containing cards for values of

$$A = \pm 1,\ \pm 2,\ \ldots,\ \pm 5,\ \pm 10,\ \ldots,\ \pm 50 \text{ and } \pm 100,\ \ldots,\ \pm 500.$$

This was done automatically by means of a tabulator coupled to a summary punch, which, in order to produce a card of amplitude $+2$, for instance, added the data on two cards of amplitude $+1$ (prepared by duplicating the original pack), rounded off by adding 0·05, and punched the result into a fresh card. The second decimal place was not retained. One consequence of this procedure is that negative numbers now appear as complements with respect to 1000. Dropping the second decimal place enabled the amplitude to be extended to 500 without requiring more than the five columns available for each entry. The overall accuracy is not decreased, as the extension of the range of amplitudes makes multiplication by rolling unnecessary (see Cox *et al.* (1947, p. 4)). Different classes of cards are distinguished by over-punches for sorting and checking, and by printed information for visual inspection. The amplitude and wave number are also printed on each card; negative values of $A$ are distinguished by having a red stripe on one corner of the card. Fig. 1 shows a typical card.

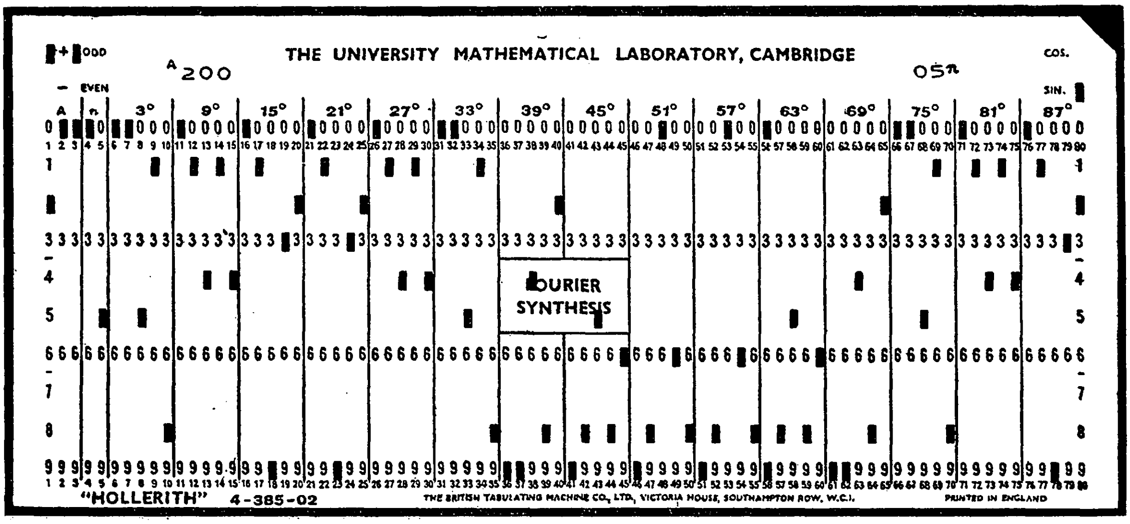

Fig. 1. A typical card.

Five duplicates of each card were prepared from the master pack, except in the case of amplitudes ± 1, 5, 50, 500 when fifteen duplicates were made. (Experience has shown that ten instead of fifteen would be sufficient.) The master pack thus contains 2460 different cards, while the working pack consists of 18,860 cards. These are filed in eight boxes, each measuring about 24 × 9 × 4 in. Cards differing only in the sign of the amplitude are filed next to one another, while cards of different amplitude and wave number are separated by coloured spacing cards. Sine and cosine functions, odd and even wave numbers, and odd and even series of 6° intervals form groups contained in the eight boxes, and these groups are never mixed. The presence of a foreign card in a pack can be detected by looking through the appropriate over-punch hole, which should make a clear channel through the pack.

The tabulator is standard Hollerith equipment and has five nine-wheel unit counters, so that the passage of a pack through the machine three times with appropriate changes of plug-board wiring is sufficient to give totals in all fifteen fields.

### Method of control-breakdown used

Control is obtained by the insertion of a control card at the required place in the pack of cards. This card also rounds off the figures standing in the counter to the nearest whole number. The control card is punched with

8 in column 4,
$X$ in column 5,
5 in the right-hand column of each degree field.

(*a*) The 8 punched in column 4 sets up Selector 1.

(*b*) The minor wander plug is plugged in the normal way.

(*c*) The $X$ punched in column 5 is read from the following card into the centre point of Selector 1. The off-side of Selector 1 is plugged to the following card section of control. The card column section of control is left blank, so that when the control card reaches the lower brushes control is broken down as $X$ is being read against blank; at all other times the two sides of control read blank against blank, so that control is not broken down.

(*d*) The 0·5 for rounding off will be added into the right-hand counter wheel from the control card, and the result will be automatically printed to the nearest whole number.

(*e*) The other fields on the card are added by altering the columns adding into the counters.

### Procedure in carrying out a synthesis

The reduction of two- and three-dimensional syntheses to a series of one-dimensional syntheses has been fully described elsewhere (Lipson & Beevers, 1936; Goodwin & Hardy, 1938). We shall therefore describe only the procedure for evaluating a number of one-dimensional syntheses, each of the form

$$f(x) = \sum_n \{C_e \cos 2nx + C_o \cos(2n+1)x + S_o \sin(2n+1)x + S_e \sin 2nx\}.$$

Assuming that the function is to be evaluated at 6° intervals of the argument $x$, the appropriate cards are drawn from the four filing boxes and are arranged as follows:

$$C_e \mid C_o \mid S_o \mid S_e \mid\mid -C_e \mid -C_o \mid -S_o \mid -S_e \mid\mid.$$

The reason for drawing two cards differing only in the sign of the amplitude will be made clear later. As these two cards are adjacent to one another the process is not slowed down appreciably by the drawing of two cards instead of one. Single vertical lines represent blank cards which enable the four classes of cards to be easily separated again. Double vertical lines represent control cards which round off the total by adding 0·5, cause the tabulator to print totals for the five fields being added, and clear the counters for the passage of the next group of cards. The figure to the right of the decimal point is not printed. The fact that a group of cards is followed by another containing corresponding cards of negative amplitude means that two totals are printed, one in direct and one in complementary form. This means that no mental arithmetic has to be done by the operator to convert negative numbers to direct form, which is particularly useful if the totals are the coefficients of a succeeding synthesis, and the zero sum of the two provides a check on the correct working of the tabulator. Cards for ten to fifteen one-dimensional syntheses are drawn at one time and passed through the tabulator in groups separated by control cards. The range of $f(x)$ is extended to $2\pi$ by rearranging the packs in the order

$$C_e \mid -C_o \mid S_o \mid -S_e \mid\mid, \text{ etc.},$$

which, on addition, gives

$$f(\pi - x) = \sum_n \{C_e \cos 2nx - C_o \cos(2n+1)x + S_o \sin(2n+1)x - S_e \sin 2nx\}.$$

$f(\pi + x)$ and $f(-x)$ are obtained similarly.

A two-dimensional synthesis of the form

$$\rho(x, y) = \sum_h \sum_k F(hk0) \cos 2\pi hx \cos 2\pi ky \quad + \text{similar terms}$$

can be evaluated at intervals of 1/60 in $x$ and $y$ by two people in about 7 hr., the time being taken up as follows:

| | hr. |
|---|---|
| Drawing cards for preliminary summation over $h$ | ½ |
| Checking | ¼ |
| Tabulating and listing (one person only) | 1 |
| Refiling cards | ½ |
| Total | 2¼ |

The final summation over $k$ takes about twice as long, the proportion of time spent on the various operations being roughly the same. It has been assumed that the series contains 200 terms of average $F$ value about 30. To evaluate the functions at intervals of 1/120 in $x$ and $y$ takes rather more than twice as long. The value of the method lies not so much in the saving of time (although this is considerable in lengthy calculations) as in the fact that, unlike methods such as those of Robertson and of Lipson & Beevers, it does not require continuous concentration on the part of the operator; the drawing and checking of cards is much less fatiguing than mental arithmetic or the operation of an adding machine, and systematic checks are more easily devised. As used at present the method is intermediate in accuracy between the 'two-figure' method of Lipson & Beevers and the 'three-figure' method of Robertson; that the former method is adequate in most instances has been shown elsewhere (Cochran, 1948). Greater accuracy could be obtained, if necessary, by multiplying all coefficients by ten, as the range of amplitudes available would still be sufficient to accommodate the numbers encountered.

The method has now been used successfully for the evaluation of a number of two-dimensional syntheses, and of one complete three-dimensional synthesis. The last, which contained over 1000 terms and was evaluated at about 6000 points, took approximately 80 hr. to complete.

Our best thanks are due to Prof. Sir Lawrence Bragg and Dr W. H. Taylor for their continued interest and support, and to Dr M. V. Wilkes for much helpful advice and for placing the facilities of the Mathematical Laboratory at our disposal. One of us (W. C.) is indebted to the Department of Scientific and Industrial Research for financial aid, and another (C. J. B. C.) to the managers of the I.C.I. Fellowship Fund of the University of Cambridge for the award of a fellowship.

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*Acta Cryst.* (1949). **2**, 116

# The Crystal Structure of Hexamethylenediamine and its Dihalides. Hexamethylenediamine Dihydrobromide

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(*Received* 13 *December* 1948)

Hexamethylenediamine dihydrobromide, $C_6H_{18}N_2Br_2$, is monoclinic, space group $P2_1/c$, with four molecules per unit cell. Only minute needle crystals were available, but the structure factors of the principal zone, (0*kl*), have been measured. A Patterson analysis determines the positions of the eight bromine atoms in this projection without ambiguity. This is followed by a two-dimensional Fourier synthesis from which the approximate positions of all the atoms can be estimated. The results are consistent with an extended chain structure of normal bond distances (1·4–1·6 A.), and with Br–N distances lying between 3·2 and 3·5 A. These results provide a basis for a more accurate determination of the structure of the isomorphous dihydrochloride.

## Introduction

Very few detailed analyses of structures involving normal aliphatic carbon chains have yet been made. In the crystalline state such chains usually occur as fully extended zigzags of carbon atoms, and are generally assumed to be regular. Careful analyses have been made for certain long-chain paraffins (Müller, 1928), and very accurate values have been obtained for the average C–C distance along the chain, but the methods employed do not lead to the inspection of individual atoms or bonds within the molecule. Recent work on the normal aliphatic dicarboxylic acids, however, has indicated certain minor but apparently significant bond-length variations extending over chains of four and even eight methylene groups (MacGillavry, 1941; Morrison & Robertson, 1949). The investigation of such effects in normal aliphatic compounds of a different type is one reason for the present series of X-ray studies on hexamethylenediamine and its dihalides.

Recently, hexamethylenediamine has also attained considerable practical importance as one of the parent substances in the preparation of numerous polyamides of high molecular weight. These substances are prepared by the condensation of hexamethylenediamine with certain dibasic acids, such as adipic or sebacic acid, and the polymers so formed constitute some of the well-known 'nylon' fibres. X-ray structural analyses of some of these fibres have been made (Bunn & Garner, 1947), but the work is necessarily difficult because of the restricted amount of diffraction data available. The present single-crystal studies of one of the parent substances may be considered as a contribution to this field as well.

Hexamethylenediamine itself is a low-melting hygroscopic solid which demands a rather special technique for its preservation during X-ray experiments. The subject has therefore been approached by a preliminary study of the easily crystalline dihalides. The relatively heavy halogen atoms in these compounds also make it possible to elucidate the molecular structure in a very direct manner by means of Patterson series.

The structure of the dihydrobromide, which is described in the present paper, has been determined only approximately, because only minute crystals were available. It has been chosen as a starting-point, however, because the heavy bromine atoms make the analysis extremely direct. The approximate parameters obtained may then be utilized in a much more comprehensive analysis of the dihydrochloride, which appears to be isomorphous with the dihydrobromide. In the analysis of the dihydrochloride, which will be described in a subsequent paper, the finer details of the chain structure are established.

## Crystal data

Hexamethylenediamine dihydrobromide, $C_6H_{18}N_2Br_2$; *M*, 278·0; m.p. 263° C.; *d*, calc. 1·656, found 1·667. Monoclinic prismatic, $a = 4{\cdot}68 \pm 0{\cdot}02$, $b = 14{\cdot}53 \pm 0{\cdot}04$,