Table 8 (cont.)

$k+l=2n-1$ (cont.)

Plane	$F_{obs.}$	$F_{calc.}$	Plane	$F_{obs.}$	$F_{calc.}$	Plane	$F_{obs.}$	$F_{calc.}$
$12\bar{5}$	<2·2	− 3·5	$46\bar{5}$	<2·4	− 4·3	$31\bar{6}$	<2·4	2·6
$14\bar{5}$	<2·2	0·2				$33\bar{6}$	<2·4	− 1·5
$16\bar{5}$	4·8	5·5	016	3·7	− 5·1			
$18\bar{5}$	4·1	− 4·9	036	<2·4	2·3	$41\bar{6}$	<2·3	1·7
$1.10.\bar{5}$	4·4	− 4·2	056	4·5	3·1			
$1.12.\bar{5}$	<2·1	− 0·1	076	<2·4	− 1·2	$51\bar{6}$	<2·0	3·0
			096	2·7	− 2·9			
$22\bar{5}$	<2·2	0·2	0.11.6	2·0	− 2·6	027	4·4	3·5
$24\bar{5}$	<2·3	2·9				047	<2·3	2·1
$26\bar{5}$	<2·3	1·2	$11\bar{6}$	<2·3	− 0·6	067	2·2	2·3
$28\bar{5}$	3·8	− 4·5	$13\bar{6}$	<2·3	− 2·2			
$2.10.\bar{5}$	<2·2	− 1·3	$15\bar{6}$	<2·3	3·3	$12\bar{7}$	<2·3	1·3
$2.12.\bar{5}$	<1·9	− 2·5	$17\bar{6}$	<2·4	− 1·6	$14\bar{7}$	<2·3	1·0
			$19\bar{6}$	<2·2	− 0·1	$16\bar{7}$	4·1	− 4·0
$32\bar{5}$	<2·3	1·0	$1.11.\bar{6}$	<2·1	1·6			
$34\bar{5}$	<2·4	1·2				$22\bar{7}$	<2·3	0·9
$36\bar{5}$	<2·4	− 1·8	$21\bar{6}$	19·2	23·5			
$38\bar{5}$	<2·4	2·3	$23\bar{6}$	<2·4	4·9	$31\bar{8}$	8·2	8·0
			$25\bar{6}$	3·4	− 4·8			
$42\bar{5}$	<2·4	− 4·5	$27\bar{6}$	7·0	− 8·3			
$44\bar{5}$	<2·4	2·4	$29\bar{6}$	<2·0	− 0·4			

The Crystal Structure of Ammonium Trinitrate, NH₄NO₃.2HNO₃

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The crystal structure of ammonium trinitrate, $NH_4NO_3.2HNO_3$, has been examined by means of X-rays, using two- and three-dimensional Fourier methods. The structure may be described as consisting of sheets containing NH_4^+ and NO_3^- ions separated by sheets containing HNO_3 molecules, with two nitric acid molecules united by hydrogen bonds to one nitrate ion. The bond lengths show, however, that this is a considerable over-simplification of the facts.

Introduction

The work of Hantzsch (1925, 1928) led him to the view that the nitration reactions of nitric acid in different solvents were due to the presence of the ions $NO(OH)_2^+$ and $N(OH)_3^{++}$. Later work has modified these views (Hughes, Ingold & Reed, 1946; Goddard, Hughes & Ingold, 1946; Bennett, Brand & Williams, 1946), and it is now established that, in sulphuric acid media, these reactions are due to the presence of the ion NO_2^+, but it is still regarded as probable that the ion $NO(OH)_2^+$ may be active in other media (Halberstadt, Hughes & Ingold, 1946). The crystal-structure analysis of ammonium trinitrate was undertaken for the information which it might give upon this topic.

Preparation of material

The system NH_4NO_3–HNO_3 was studied by Groschuff (1904), who investigated the conditions necessary for the isolation of ammonium trinitrate; our preparation was based upon the phase diagram published by him.

Anhydrous nitric acid in a pure state was prepared by vacuum-distillation of pure nitric acid ($d = 1·42$, 10 vol.) with concentrated sulphuric acid ($d = 1·84$, 13·2 vol.) in an all-glass apparatus. The pure nitric acid, of not less than 99·9 % purity, which was collected in a receiver cooled in ice-water, was stored in the dark in a refrigerator; under these conditions the acid remained colourless for periods of months.

Ammonium nitrate of 'Analar' grade was powdered and dried at 100° C. for several days, being frequently stirred, and was finally kept over phosphorus pentoxide for several weeks before use.

In order to be able to isolate and preserve single crystals of the trinitrate, it was found necessary to take the most stringent precautions to exclude moisture, and to avoid conditions in which nitric acid vapour might decompose. For the preparation, 2·50 g. of ammonium nitrate and 7·50 g. nitric acid were mixed in a stoppered flask and transferred to the crystal isolation apparatus, consisting of a boiling tube through which

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a stream of air was passed; this air had been dried with phosphorus pentoxide, and brought to equilibrium with solid ammonium trinitrate. Crystallization was induced with 'Drikold', and the solution was stirred and allowed to stand. A suitable crystal was selected using a binocular microscope and drained on a vacuum filter in the boiling tube. It was then mounted on a glass fibre and transferred without contact with external air to a small polythene container which was then mounted on the goniometer.

Polythene was chosen as the material for the enclosing tube, as it is unaffected by nitric acid and is very transparent to copper K radiation. The container, which was cylindrical, had a wall thickness of 0·3 mm., uniform to 0·01 mm.; it contained 'anhydrone' to act as a desiccant and some solid ammonium trinitrate to maintain the vapour pressure of nitric acid within. The fibre support was so arranged that the crystal was in its correct position on the axis of the container, which in use was not allowed to deviate from an axis-vertical position by more than c. 3°. Under these conditions, differences in absorption by the container walls of diffracted beams of a given layer line were so small that they could be neglected. Polythene is crystalline and gives a strong powder pattern when exposed to X-rays, but no difficulty was experienced in making a suitable allowance for this when relative intensities were being measured; also, it is not transparent to light, and preliminary adjustment of the crystal had to be carried out by viewing the crystal in a measuring microscope through a small glass window in the end of the container, and bringing it to a predetermined height relative to the goniometer.

These operations were carried out in a room lit only by artificial light, to avoid photochemical decomposition of nitric acid, and subsequently the crystal was kept in the dark except for brief periods when the camera was being changed. A current of dry hydrogen was passed through the camera to exclude moisture.

Preliminary crystallographic examination

Three series of single crystal 15°-oscillation photographs were taken using Cu $K\alpha$ radiation (Ni filter); the crystals were oscillated about the crystal axes, covering 90° about [a] and [b] and 180° about [c]. The axes were found to be

$$a = 6·57, \quad b = 12·64, \quad c = 4·56 \text{ A.}$$

($\lambda(\text{Cu } K\alpha) = 1·542$ A.). Absent reflexions were (i) odd orders of 00l, (ii) odd orders of 0k0, with the exception of a weak 010 reflexion. From these results, and the symmetry of all oscillation photographs about the equator line, the crystal was considered to be monoclinic, pseudo-orthorhombic; and the space group to be $P2_1$ very slightly distorted from $P22_12_1$; the only evidence for this slight distortion is the weak 010 reflexion. Orthogonality of the lattice in planes perpendicular to the [c] axis (the true 2_1 axis) was checked by recording

on one film, without disturbing the camera, the four equatorial reflexions of type 6,11,0; they coincided in pairs, and it was concluded that any distortion of angle γ from 90° was less than 10 sec. of arc, if it existed at all. Comparison on [c]-axis films of intensities of reflexions arising from adjacent quadrants of the reciprocal lattice showed no departure from orthorhombic symmetry. The very close approach of the space-group symmetry to $P22_12_1$ led to the choice of $P2_1$ as the true space group, since these two symmetry groups can lead to similar structures which can be derived from each other by minor displacements. The orthorhombic space group $P222_1$ is also possible from the extinction and symmetry data, but was rejected since it would require an entirely different structure from that required by $P22_12_1$.

An approximate measurement of density gave a value of 1·76 g.cm.$^{-3}$; this measurement was made by synthesis of some salt in a specific gravity bottle followed by the use of a displacement method, since crystals always adhered to the walls of the container when a flotation method was tried. This value for the density leads to a value of $n = 2$ units of NH₄NO₃.2HNO₃ per unit cell.

Measurement of intensities

Film processing was carried out under standardized conditions at 18° C.

Intensities of reflexions were estimated visually from oscillation photographs (see above) by means of a standard scale of spots of known exposure ratio. Spots which were too intense for estimation were reduced in intensity by the use of aluminium foil screens. The recorded intensities ranged from 1 to 5500 on an arbitrary scale. The visual comparison was carried out with extreme care, on an oal screen in a darkened room, using a headband-type magnifier, which was found greatly to facilitate the work. The usual corrections were applied for angular-velocity effects and polarization by means of the expression $F^2 = kIDp/L$, where D is the Cox & Shaw factor, p the polarization factor and L the Lorentz factor; all reflexions were then brought to the same arbitrary scale by means of a process of systematic comparison and averaging. The effects of absorption were minimized by the use of small crystals of approximately square section, and no absorption correction was applied. Finally, a table of relative structure amplitudes ($F_{\text{obs.}}$) was constructed.

Determination of the structure

The structure was treated as though its space group were $P22_12_1$. This space group accommodates four asymmetric units in general positions or two twofold axially symmetric units situated on twofold axes. The NH₄⁺ and NO₃⁻ ions were assigned to positions on the twofold axes and the HNO₃ molecules to general positions. Two of the oxygen atoms of NO₃⁻ will not

lie on the twofold axis and are equivalent to one oxygen atom in a general position; it is necessary therefore to determine eighteen parameters to define the structure. It was found that the possible orientation of the nitrate ion was limited by approach of O_{11} and O_{12} to NH_4^+ ions (see Fig. 2). Attention was focused upon the $0k0$ and $00l$ reflexions, and structure amplitudes were calculated for the 'NH_4NO_3' part of the unit cell for a series of positions within the narrow range of movement permitted to the 'NO_3^-' ion. Structure amplitudes were then calculated for the 'HNO_3' part of the unit cell, making reasonable assumptions regarding the positions of the atoms. A comparison of these two sets of structure amplitudes with the observed values enabled the signs of the 040, 060 and 002 reflexions to be correctly deduced, and indicated the likely arrangement of HNO_3 molecules. From this preliminary model of the unit cell, calculations of $0kl$ structure amplitudes were made, followed by adjustments of parameters, until a tolerable measure of agreement between observed and calculated structure amplitudes was obtained; Bragg charts were employed in deciding the movements of different atoms which were necessary to improve the agreement. A series of two-dimensional Fourier projections on (100) was then made, but the resolution of atoms of the HNO_3 molecule did not enable a choice to be made between two possible orientations. A Patterson F^2 synthesis projected on (100) was next carried out, and it was found possible by its aid to decide upon the general orientation of this group, and further refinement was continued by means of two-dimensional Fourier projections. It was then found possible to assign approximate z co-ordinates in a unique manner, and a similar process of refinement was carried out by two-dimensional Fourier projections on (001).

The parameters of the atoms were then further refined by means of four complete sets of three-dimensional Fourier lines parallel to the [a] axis, and sections parallel to (100) using all hkl reflexions (Fig. 1) (452 terms observed).

Finally, an average atomic scattering curve was drawn, and structure amplitudes were calculated, making the assumption that

$$f(\text{oxygen}):f(\text{nitrogen}):f(NH_4^+)=8:6:6,$$

where f is the atomic scattering factor; it was found that this ratio was in best agreement with the results. Comparison of the experimental scattering curve with the theoretical curve showed that the experimental structure amplitudes were already on an approximately absolute scale; they were therefore treated as absolute for drawing contour maps of electron density. Since the observed and calculated amplitudes are on the same scale, the fact that the scale is not quite absolute will not affect the value of the expression

$$\frac{\Sigma\,||\,F_{\text{obs.}}\,|-|\,F_{\text{calc.}}\,||}{\Sigma\,|\,F_{\text{obs.}}\,|},$$

which was found to be 0·18.

Following the suggestion of Booth (1946), the probable systematic error of the parameters, due to termination of series, was estimated by carrying out a two-dimensional Fourier projection on (100) using calculated values of the structure amplitudes, and measuring the resulting movements of the atoms; the z co-ordinates were assumed to be subject to the same errors as were revealed for the x and y co-ordinates.
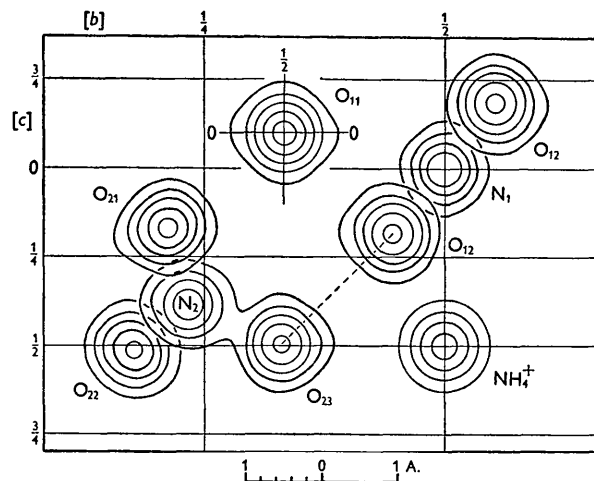
Fig. 1. Composite three-dimensional Fourier section of the unit cell by a series of planes, parallel to (100), which pass through the centres of atoms; contours are at equal intervals of approximately 2 e.A.$^{-3}$. O_{11} is displaced to reveal N_1 and O_{12}, and hydrogen-bonded atoms are shown linked by a broken line.

Results of the analysis and description of the structure

The atomic parameters are summarized in Table 1.

Table 1. *Atomic parameters*

	x	y	z
Special positions:			
NH_4	0·120	0	0
N_{11}	0·389	$\frac{1}{2}$	0
O_{11}	0·208	$\frac{1}{2}$	0
General positions:			
O_{12}	0·489	0·447	0·185
N_2	0·223	0·234	0·386
O_{21}	0·324	0·213	0·170
O_{22}	0·107	0·177	0·515
O_{23}	0·237	0·331	0·496

Substitution of the parameters in the co-ordinates of the point positions of space group $P22_12_1$ (*International Tables*) gives the position of every atom in the unit cell. Fig. 2 shows the disposition of the atoms in the structure and the calculated bond lengths and interbond angles. The probable error of bond lengths is estimated to be $\pm0·02$ A. The structure consists essentially of sheets containing NH_4^+ and NO_3^- ions, between which are sheets containing the HNO_3 molecules, but the bond lengths show that this simple description can be used only for focusing ideas; for simplicity, this description will be used in the following discussion.

The nitrate ion does not possess a threefold symmetry axis but is planar, being situated with the N_1 and O_{11} atoms on a twofold axis of symmetry. The bond lengths and angles may be compared with those observed in the nitrate ion in sodium nitrate (Elliott, 1937), namely, $N-O = 1.21$ A. and $\angle O-N-O = 120°$. The difference observed in the present case is attributed to the formation of two hydrogen bonds, joining each nitrate ion to two nitric acid molecules; the presence of these hydrogen bonds is shown by the small separation (2.63 A.) of O_{12} of the nitrate ion and O_{23} of a nitric acid molecule.

The NH_4^+ ion has twelve oxygen atoms as nearest neighbours, in a deformed close-packed arrangement, the observed NH_4^+-O distances being 3.01, 3.10, 3.13, 3.14, 3.17, 3.24 A. It appears that a weak hydrogen bond exists between NH_4^+ and O_{12} (separation 3.01 A.), but for the remainder, conclusions regarding such bonding are less certain. On stereochemical grounds it seems probable that only three hydrogen bonds can be formed by NH_4^+ at one time, and possibly a selection process occurs between possible orientations, which may be fixed during crystal formation or may undergo change
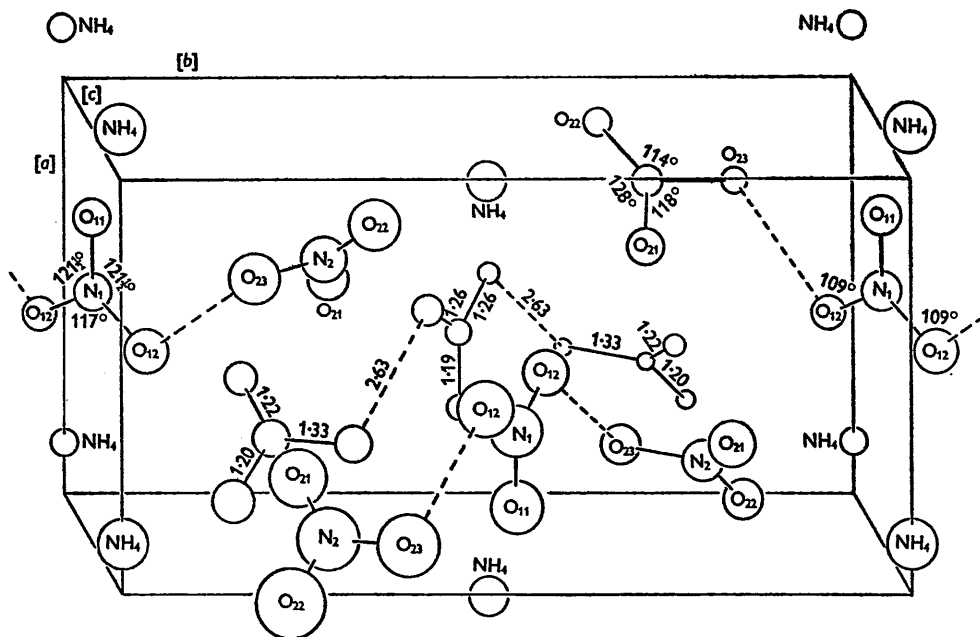

Fig. 2. The atomic arrangement in the crystal. The unit cell is outlined, and stereoscopic effect is gained by assigning to an atom a diameter depending only upon its z co-ordinate. The nearest and further HNO_3 molecules lie wholly outside the unit cell shown. Lengths are ± 0.02 A.

The HNO_3 molecule is planar (calculated distance of N_2 from plane of $O_{21}-O_{22}-O_{23} = 0.005$ A.) and two oxygen atoms are equivalent ($N_2-O_{21} = 1.20$, $N_2-O_{22} = 1.22$ A.) within the limits of experimental error. The remaining oxygen atom O_{23} has a greater separated from the nitrogen atom (1.33 A.) and is considered to be the –OH oxygen; this view is supported by the observation of hydrogen-bond formation between this atom and O_{12} of the nitrate ion. These results may be compared with the values obtained by Maxwell & Mosley (1940) from an electron-diffraction study of nitric acid vapour, namely,

$$N-O = 1.22 \pm 0.02, \quad N-OH = 1.41 \pm 0.02 \text{ A.}$$

There is no significant difference between the N–O values, but the different N–OH bond length is again attributed to the influence of hydrogen-bond formation involving the –OH group.

The following distances are observed between the remaining non-bonded oxygen atoms: 3.04, 3.11, 3.14, 3.15, 3.15, 3.17, 3.22, 3.23, 3.25, 3.27, 3.31, 3.33 A.

with time. The likely manners in which such a system of hydrogen bonds could be formed involve orientations of the NH_4^+ ion such that it does not possess a twofold symmetry axis coinciding with that required by space group $P22_12_1$. Therefore, the deformations produced in neighbouring groups will not conform to the space-group symmetry, which will be lowered to that of a monoclinic or even triclinic space group; this effect would probably be small for such weak hydrogen bonds. The strong 062 reflexion is accompanied by considerable diffuse scattering; the 062 plane coincides almost exactly with the plane of the nitrate ion situated on the twofold axis, and it seems likely that the diffuse scattering arises from the thermal vibrations of this group. These thermal vibrations will destroy the twofold symmetry of this axis, and will therefore result in a lowering of the space-group symmetry. These two effects are thought to account for the weak 010 reflexion.

Dr F. J. Wilkins suggested the subject of this work, and his interest and encouragement are gratefully

acknowledged; it was completed early in 1948 and forms part of a programme of fundamental research sponsored by the Ministry of Supply at the University of Birmingham. Approval for publication has been granted by the Chief Scientist, Ministry of Supply.

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Table 2. *Observed and calculated structure amplitudes*

hkl	$F_{obs.}$	$F_{calc.}$	α (°)	hkl	$F_{obs.}$	$F_{calc.}$	α (°)	hkl	$F_{obs.}$	$F_{calc.}$	α (°)
(010)	(1·8)	—	—	034	1·3	0·0	0	172	3·8	4·2	304
020	11·5	16·9	180	044	2·8	1·6	180	182	6·1	8·5	175
040	27·2	39·3	0	054	4·2	7·1	0	192	1·6	2·0	281
060	24·6	28·1	0	064	13·8	14·5	0	1.10.2	2·5	1·9	146
080	4·6	8·6	180	074	—	1·2	0	1.11.2	3·2	1·5	261
0.10.0	1·1	2·1	0	084	1·0	1·5	180	1.12.2	1·7	1·8	276
0.12.0	7·5	7·0	0	094	—	0·0	—	1.13.2	2·1	4·2	219
0.14.0	2·1	1·2	0	0.10.4	2·6	2·8	0	1.14.2	1·9	1·9	125
0.16.0	1·5	2·2	0								
				015	1·7	3·1	180	103	8·7	10·6	270
011	13·1	16·7	180	025	1·8	1·8	0	113	6·6	7·0	216
021	4·7	3·4	0	035	4·0	4·7	180	123	19·6	19·3	81
031	15·7	16·4	180	045	2·8	4·8	180	133	6·0	5·0	65
041	25·3	27·9	0	055	1·3	0·8	0	143	10·7	10·6	83
051	5·3	7·2	180	065	1·6	1·8	0	153	5·9	4·6	309
061	3·9	3·8	180	075	3·3	1·2	180	163	5·2	4·6	293
071	1·3	0·0	180	085	2·2	1·8	0	173	5·3	4·3	47
081	14·0	15·4	0					183	9·8	12·2	82
091	3·3	2·1	180	100	7·2	8·3	180	193	7·6	9·3	348
0.10.1	6·5	8·0	180	110	8·7	11·1	270	1.10.3	2·3	2·2	128
0.11.1	1·5	1·1	180	120	17·0	20·3	180	1.11.3	1·9	1·2	49
0.12.1	1·6	0·6	0	130	15·9	18·0	270	1.12.3	0·8	1·5	89
0.13.1	1·8	0·6	180	140	8·4	9·3	180	1.13.3	1·9	2·5	353
0.14.1	2·7	3·5	180	150	9·5	10·1	90				
0.15.1	3·5	0·7	180	160	15·1	17·8	0	104	4·1	5·4	0
				170	19·5	25·0	270	114	6·0	6·3	222
002	32·4	32·2	0	180	4·2	4·9	0	124	1·8	1·9	166
012	6·5	6·6	180	190	11·0	11·4	90	134	2·9	3·1	138
022	1·7	0·7	180	1.10.0	3·4	5·0	0	144	2·7	2·2	258
032	7·3	9·1	180	1.11.0	7·7	8·1	270	154	6·5	3·9	234
042	2·3	2·1	0	1.12.0	5·8	7·9	0	164	3·4	4·3	40
052	4·9	3·6	180	1.13.0	—	0·5	270	174	2·5	3·6	179
062	30·7	34·3	0	1.14.0	2·1	3·3	180	184	2·4	4·1	237
072	9·3	10·4	180	1.15.0	1·2	0·7	270	194	2·1	2·4	287
082	5·1	4·6	0					1.10.4	1·3	2·6	74
092	5·6	5·0	0	101	16·1	15·0	270	1.11.4	1·5	0·7	54
0.10.2	4·5	6·1	0	111	30·9	26·8	290				
0.11.2	3·0	2·6	180	121	40·5	40·1	100	105	2·7	2·0	90
0.12.2	10·7	13·5	0	131	32·9	32·4	35	115	3·9	4·4	50
0.13.2	2·4	4·4	0	141	31·1	29·1	133	125	1·8	2·4	61
0.14.2	1·1	2·1	180	151	11·9	13·2	244	135	4·0	5·2	332
				161	5·8	6·6	206	145	5·4	6·6	82
013	1·4	2·5	0	171	5·3	5·3	37	155	1·6	1·4	121
023	—	0·2	180	181	13·0	14·8	114	165	1·3	2·8	280
033	1·8	4·0	0	191	3·4	2·4	7				
043	2·3	3·7	180	1.10.1	10·4	10·6	80	200	21·4	27·4	180
053	8·0	10·4	180	1.11.1	1·3	2·6	224	210	15·4	15·7	90
063	4·3	3·0	180	1.12.1	4·1	5·0	302	220	27·2	37·3	0
073	1·6	0·4	180	1.13.1	2·3	2·7	59	230	3·4	3·3	90
083	2·3	2·0	0	1.14.1	6·4	7·5	74	240	11·4	10·9	180
093	5·3	8·9	180	1.15.1	3·1	2·5	324	250	7·9	7·0	90
0.10.3	3·0	2·7	180					260	9·9	10·1	180
0.11.3	2·4	4·2	180	102	27·9	27·6	0	270	11·5	10·5	90
0.12.3	2·4	2·7	0	112	12·6	13·5	309	280	9·0	9·8	180
0.13.3	1·0	0·2	0	122	4·8	4·1	253	290	3·8	5·6	270
				132	4·7	4·3	49	2.10.0	3·5	5·3	180
004	8·7	10·3	0	142	5·7	6·7	68	2.11.0	5·8	6·5	90
014	5·6	6·0	0	152	14·6	15·2	319	2.12.0	5·3	5·7	180
024	8·2	6·0	0	162	5·9	5·8	331	2.13.0	2·8	0·7	90

A C 3

Table 2 (cont.)

hkl	$F_{obs.}$	$F_{calc.}$	α (°)	hkl	$F_{obs.}$	$F_{calc.}$	α (°)	hkl	$F_{obs.}$	$F_{calc.}$	α (°)
2,14,0	1·3	1·1	180	3,10,0	5·8	6·9	0	401	1·8	0·6	90
				3,11,0	8·1	10·3	90	411	3·9	3·8	293
201	24·8	25·8	270	3,12,0	3·7	4·7	180	421	13·0	12·0	294
211	16·0	14·7	135	3,13,0	0·8	0·7	270	431	16·5	18·6	166
221	31·8	26·9	58	3,14,0	2·1	3·0	0	441	7·1	6·8	2
231	23·1	19·9	349					451	5·3	4·8	13
241	5·2	4·4	30	301	13·0	11·1	90	461	7·3	7·9	310
251	4·2	4·6	147	311	12·2	10·9	51	471	6·1	4·9	360
261	17·6	18·9	340	321	11·2	13·1	181	481	3·6	2·0	345
271	3·7	3·5	63	331	11·8	10·1	240	491	7·8	9·0	163
281	8·1	10·1	109	341	7·1	5·8	116	4,10,1	2·7	1·9	241
291	12·0	13·5	347	351	7·8	6·6	15	4,11,1	5·3	6·9	334
2,10,1	3·9	3·2	6	361	11·8	13·0	180	4,12,1	1·7	2·2	240
2,11,1	3·1	3·0	126	371	7·3	8·3	198	4,13,1	0·9	2·0	127
2,12,1	4·2	4·8	192	381	5·7	4·8	74				
2,13,1	2·3	3·2	315	391	1·5	0·7	61	402	4·9	6·0	180
2,14,1	1·5	2·8	118	3,10,1	1·5	2·8	252	412	6·8	7·3	41
2,15,1	1·4	1·7	33	3,11,1	2·9	2·4	182	422	9·7	9·6	208
				3,12,1	3·6	3·4	47	432	9·3	9·3	179
202	19·4	20·1	180	3,13,1	—	0·7	117	442	5·9	5·9	133
212	13·1	12·5	122	3,14,1	2·6	2·9	15	452	4·0	3·9	111
222	7·8	8·4	169					462	6·4	6·4	262
232	8·9	7·8	246	302	11·1	9·7	180	472	7·5	7·4	116
242	5·2	5·7	267	312	17·5	15·8	123	482	4·3	4·1	72
252	16·8	17·6	125	322	9·0	10·2	356	492	1·6	1·4	276
262	8·5	8·6	142	332	21·8	19·7	317	4,10,2	2·9	2·8	255
272	3·0	0·9	114	342	3·6	4·7	134	4,11,2	4·0	4·7	83
282	5·3	6·5	297	352	9·9	11·7	90				
292	5·0	4·2	154	362	7·7	7·8	187	403	8·6	7·7	270
2,10,2	5·3	5·7	42	372	6·4	5·9	38	413	7·5	8·0	20
2,11,2	5·2	5·8	44	382	3·1	2·9	140	423	3·9	4·7	117
2,12,2	3·0	3·5	206	392	6·3	6·6	279	433	8·4	8·5	164
2,13,2	1·9	0·8	110	3,10,2	4·1	5·1	194	443	6·4	5·6	273
2,14,2	1·1	1·1	26	3,11,2	3·8	5·2	119	453	3·9	5·1	8
				3,12,2	2·1	2·6	161	463	4·1	2·7	205
203	2·0	1·7	90					473	2·3	3·3	194
213	5·4	6·2	357	303	2·2	0	360				
223	1·3	1·7	126	313	8·9	9·1	143	404	4·5	2·8	180
233	11·9	12·9	5	323	3·7	2·2	59	414	4·2	3·4	55
243	9·3	8·7	114	333	4·5	3·1	266	424	1·6	1·4	99
253	2·6	2·5	263	343	1·3	1·9	324	434	2·5	2·4	1
263	5·5	5·7	270	353	5·1	4·3	159	444	4·6	3·3	193
273	4·0	5·2	160	363	5·2	4·2	58	454	3·0	3·2	54
283	5·0	4·4	122	373	4·8	6·5	358	464	1·1	2·5	80
293	2·7	3·2	342	383	—	1·4	120				
2,10,3	2·8	2·4	44	393	1·7	1·1	143	405	2·4	1·4	270
2,11,3	1·7	3·5	181	3,10,3	1·7	1·3	38	415	1·3	1·6	109
2,12,3	2·1	3·2	260								
				304	3·9	4·2	180	500	6·6	8·3	180
204	0·9	1·1	180	314	4·4	5·2	65	510	8·4	8·5	270
214	5·2	4·6	123	324	1·0	1·5	277	520	2·2	1·9	0
224	5·3	4·6	210	334	7·2	8·1	230	530	6·0	6·8	90
234	4·5	6·3	345	344	1·2	0·9	119	540	5·3	2·6	0
244	6·2	5·4	52	354	5·1	6·4	113	550	6·0	6·9	270
254	4·0	5·6	60	364	2·9	4·1	205	560	1·0	0·4	0
264	6·0	6·3	202					570	1·6	0·1	270
274	2·5	2·3	26	305	0·9	0·2	270	580	9·4	10·0	0
284	2·1	2·0	44	315	2·1	2·2	6	590	4·7	3·4	90
				325	2·2	2·7	69	5,10,0	2·3	1·1	0
205	1·9	3·1	270	335	1·0	0·9	92	5,11,0	2·3	2·0	270
215	2·3	3·2	188					5,12,0	3·2	3·8	0
225	2·3	3·1	122	400	3·2	8·7	0				
235	3·4	3·9	10	410	14·0	14·7	90	501	8·5	9·7	270
245	2·0	1·1	80	420	2·1	0·3	0	511	4·5	5·4	157
255	1·4	2·3	210	430	0·8	4·3	270	521	6·2	6·0	113
				440	1·5	0·7	180	531	11·6	11·5	192
300	17·8	21·2	180	450	11·4	13·9	90	541	6·5	6·7	199
310	12·6	12·9	90	460	9·8	8·3	180	551	6·9	4·0	204
320	20·5	18·4	180	470	1·8	0·4	270	561	3·1	3·5	238
330	17·5	17·4	270	480	1·7	3·3	180	571	3·5	2·2	180
340	2·9	2·2	180	490	1·4	0·6	90	581	2·1	2·8	191
350	8·2	11·7	90	4,10,0	7·7	9·1	180	591	9·9	10·9	189
360	5·2	4·9	180	4,11,0	3·7	3·0	90	5,10,1	—	1·1	357
370	11·3	9·0	90	4,12,0	1·8	0·9	180	5,11,1	1·9	2·1	70
380	3·6	2·9	0	4,13,0	—	0·3	90				
390	10·3	10·6	270	4,14,0	1·9	1·3	180	502	5·0	5·4	0

Table 2 (cont.)

hkl	$F_{obs.}$	$F_{calc.}$	α (°)	hkl	$F_{obs.}$	$F_{calc.}$	α (°)	hkl	$F_{obs.}$	$F_{calc.}$	α (°)
512	8·0	8·3	344	6,11,0	5·9	5·9	270	720	0·9	0·2	0
522	5·9	5·6	26					730	2·1	2·2	270
532	5·3	3·4	123	601	0·9	0·2	270	740	3·8	3·0	180
542	5·7	5·0	338	611	2·3	1·2	197	750	—	1·3	90
552	6·5	5·7	338	621	5·3	3·1	80	760	1·4	0·2	0
562	3·8	4·3	107	631	3·0	2·3	112	770	—	0·7	270
572	4·4	4·3	285	641	4·9	5·7	355	780	1·8	0·7	0
582	2·7	2·9	299	651	2·0	2·5	15				
592	2·2	2·8	88	661	5·1	3·9	86	701	5·1	6·7	90
5,10,2	1·5	1·9	101	671	2·6	2·4	138	711	3·8	3·6	316
				681	2·0	2·6	355	721	6·7	6·4	259
503	—	1·1	270	691	4·3	3·6	348	731	3·9	3·9	6
513	6·4	4·6	205	6,10,1	1·7	2·3	113	741	4·0	3·5	213
523	2·6	3·6	264					751	2·7	2·1	316
533	11·7	12·3	171	602	9·2	10·6	180	761	1·1	2·3	114
543	2·9	3·4	42	612	9·0	8·5	237	771	1·7	1·2	269
553	—	2·3	348	622	1·9	2·3	17	781	3·5	4·5	249
563	3·2	3·4	264	632	2·9	1·7	327				
				642	3·2	3·0	257	702	0·7	0·8	180
504	—	0·4	180	652	6·7	7·0	233	712	2·6	1·1	168
514	2·7	2·1	238	662	3·9	3·8	161	722	1·3	1·3	6
524	3·4	3·2	338	672	3·7	3·9	264	732	3·4	3·1	26
534	2·9	2·4	120	682	2·7	4·1	332	742	1·7	2·0	90
544	—	0·7	23								
				603	5·0	5·1	90	703	1·0	0·7	270
600	2·7	1·4	180	613	2·7	2·7	302	713	1·3	1·0	162
610	7·7	6·6	270	623	0·8	0·9	201				
620	5·1	3·9	0	633	4·1	4·2	17	800	6·5	4·3	0
630	1·2	1·2	90	643	2·9	2·8	103	810	1·1	0·8	90
640	1·0	3·0	0	653	2·2	2·6	205	820	1·4	1·9	0
650	7·5	8·2	270					830	2·1	2·4	90
660	5·2	6·8	180	604	2·9	3·4	180				
670	6·7	5·7	270	614	4·2	4·0	303	801	3·0	2·3	90
680	2·9	1·6	180					811	3·2	2·8	88
690	1·1	0·7	270	700	8·1	8·3	180	821	3·9	1·3	299
6,10,0	—	0·1	180	710	2·5	1·2	270				

Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.

A new punched-card method of Fourier synthesis. By D. M. S. GREENHALGH and G. A. JEFFREY, *Department of Inorganic and Physical Chemistry, University of Leeds, England*

In the Hollerith methods for summing Fourier series which have been described hitherto (e.g. Cox, Gross & Jeffrey, 1947) the punched cards have been essentially more accurate Beevers–Lipson strips. It was possible to reduce the number of cards by using the technique of 'progressive digiting', and subsequently we found that further advantages could be obtained by expressing the amplitudes in the binary scale and using the feature of the B.T.M. Rolling Total Tabulator whereby a counter can be added into itself to double its contents; nevertheless, all methods retained an undesirable feature of the original Beevers–Lipson procedure, namely, the preliminary selection of cards from a filing system. Hand selection requires careful checking, and ultimately the cards must be refiled and again checked; these are tedious and time-consuming operations, however well they are organized.

This note outlines the principles of a new method which has been developed by one of us (D. M. S. Greenhalgh) and which has the great advantage that hand selection and filing of cards have been eliminated. Full technical details are being published elsewhere (Greenhalgh, 1950). For the first stage of a synthesis, the appropriate amplitudes A_n are hand-punched on to the relatively small number of cards required, and for subsequent stages the amplitudes can be summary-punched from the results of the preceding summations. The trigonometric functions are represented in the binary scale in the way described below, and are transferred to these cards from a master pack. The whole set of cards can be stored afterwards as a compact and permanent record of the job.

All the arithmetical operations in a synthesis by the new method are performed in the ordinary decimal scale on the