diagrammes d'oscillation jusqu'à −100° C. environ. Aucun changement de structure a été observé.

Propriétés physiques

Les cristaux possèdent un plan de clivage très prononcé perpendiculaire à l'axe *c*. En effet, la structure montre que dans cette direction la liaison entre les ions est beaucoup plus faible que dans la direction *a*.

Par suite de la grande hygroscopicité et de la réactivité chimique de ce composé il est impossible d'observer les cristaux sous le microscope polarisant ni à l'air, ni dans une goutte d'huile de paraffine. Pourtant des mesures optiques ont pu être effectuées, les cristaux étant mis dans un appareil de verre décrit auparavant (de Decker & MacGillavry, 1941) dans lequel on souffle un courant d'air séché. Un cristal observé en lumière parallèle, dans une direction perpendiculaire à l'axe du prisme, montre une extinction droite, la vibration d'indice le plus petit étant dirigée parallèlement à l'axe *c*.

En raison des dimensions de l'appareil il a été impossible d'employer le grossissement le plus fort pour obtenir une figure d'interférence en lumière convergente. Cependant une telle figure a été observée par hasard, très claire et parfaite, avec un grossissement plus faible et sans lentille de Bertrand. Le cristal observé, qui était coupé perpendiculairement à l'axe *c*, était recouvert d'une petite goutte de liquide, formée par attraction d'un peu d'eau. Evidemment cette goutte de liquide agissait comme une lentille additionnelle. Le cristal se trouve être uniaxe et *négatif*.

Les auteurs désirent témoigner leur reconnaissance à Mlle. Caroline H. MacGillavry pour ses conseils pendant le travail et pendant la rédaction du manuscrit.

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The Crystalline Structure of Isatin

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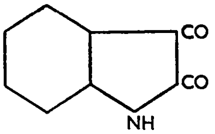
The crystalline structure of isatin has been completely elucidated by means of three-dimensional Fourier syntheses utilizing the {*hkl*} diffracted beams obtainable with Cu $K\alpha$ radiation. The molecules lie in a plane at 9° with $(10\bar{2})$ and at 1° with [*b*] and are linked in pairs across a symmetry centre by two hydrogen bonds of length 2·93 A. The interatomic bond distances show that the lactam structure predominates.

Introduction

The crystal structure of isatin has been previously investigated by Cox, Goodwin & Wagstaff (1936); their structure, obtained from the measurement of seventeen structure amplitudes and from packing considerations, is substantially correct, but is insufficiently accurate to describe unequivocally any of the inter- and intra-molecular distances. Earlier chemical and spectral investigations (Hartley & Dobbie, 1899; Morton & Rogers, 1925; Ault, Hirst & Morton, 1935) failed to distinguish between the lactam (I) and lactim (II) structures,



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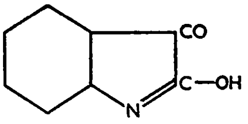

II

and the crystallographic work of Cox *et al.* represents the first crystallographic attempt to resolve this problem. The investigation reported in this paper is complete in that the atomic positions have been determined by means of three-dimensional Fourier sections and line syntheses, with an estimated accuracy of ± 0·02 A.

Preliminary crystallographic data

Groth describes the crystal of isatin as elongated monoclinic prismatic combinations of *m*{110} and *b*{010} terminated by *q*{011} or $r\{10\bar{2}\}$; the crystals exhibit good cleavage parallel to $r\{10\bar{2}\}$. The axial ratios are $a:b:c=0{\cdot}4251:1:0{\cdot}5025$, $\beta=94°42'$ and the plane of the optic axis is *b* (010). Cox *et al.* (1936) confirmed these data, measured the three refractive indices (with yellow light), and determined the cell dimensions and space group as follows:

$\alpha=1{\cdot}46\pm0{\cdot}005$ perpendicular to $r\,(10\bar{2})$,
$\beta=1{\cdot}80\pm0{\cdot}03$ perpendicular to *b* (010),
$\gamma=1{\cdot}90\pm0{\cdot}03$ parallel to [201].

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The birefringence is negative and a centred acute-bisectrix figure is visible through $r\,(10\bar{2})$.

$[a]=6{\cdot}19$, $[b]=14{\cdot}55$, $[c]=7{\cdot}19$ A., whence

$$a:b:c=0{\cdot}4254:1:0{\cdot}4941,\quad \beta=95^\circ\,00'.$$

Space group $P2_1/c$–C^5_{2h}. Four molecules per unit cell.

We have confirmed the goniometric and optical data, and using single-crystal rotation photographs and Cu $K\alpha$ X-radiation obtain the cell dimensions

$$[a]=6{\cdot}19,\quad [b]=14{\cdot}46,\quad [c]=7{\cdot}17\text{ A.};\quad \beta=94^\circ\,49'.$$

The displacement of the molecular plane from the $(10\bar{2})$ plane determined by the final atomic co-ordinates opened the question as to whether the direction of maximum refractive index lay in the direction found by Cox or in the plane of the molecule. The extinction angle is 71·5° with the $[c]$; [201] makes an angle of 64° and the plane of the molecule 73° with the $[c]$, indicating that the true direction of γ is parallel to the molecular plane.

Determination of the structure

The intensities of nearly all the diffracted beams obtainable using Cu $K\alpha$ X-radiation were determined from single-crystal oscillation photographs about $[a]$, $[b]$, $[c]$, and the structure amplitudes were computed and correlated by the method described by Llewellyn (1947). These structure amplitudes, together with those calculated from the final atomic co-ordinates, are listed in Table 8.

From the high negative birefringence, the great intensity of the $10\bar{2}$ diffracted beam, and the spacing of the $10\bar{2}$ planes (3·25 A.), Cox inferred that the isatin molecule must be flat, or nearly so, and that it must lie approximately parallel to the $10\bar{2}$ plane, two molecules being arranged about the symmetry centre as shown in Fig. 1. Following this we constructed a flat molecular model having the following dimensions:

C–C (benzene ring)	$=1{\cdot}39$ A.	C_2–N $=1{\cdot}34$ A.
C–C (heterocyclic ring)	$=1{\cdot}49$ A.	C–$O_2=1{\cdot}25$ A.
C_8–N	$=1{\cdot}47$ A.	C–$O_3=1{\cdot}21$ A.

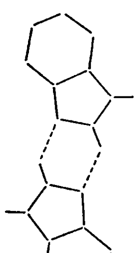


Fig. 1. The disposition of two isatin molecules about a symmetry centre. The broken lines indicate the hydrogen bonding.

Two molecules were so disposed about the centre of symmetry that they lay in the $10\bar{2}$ plane, the $N\cdots H\cdots O$ distance approximated to 2·76 A., and the atom C_7 lay on the $[b]$ axis. By means of Bragg charts the structure amplitudes of the planes 020, 040, 121, 202, 212 were calculated for various positions of the molecule in the neighbourhood of that reported by Cox. These planes all lie in the $[10\bar{1}]$ zone, but since the angle between $(10\bar{2})$ and $(10\bar{1})$ is small very little distortion arises from projecting the flat molecule on to the $(10\bar{1})$ plane, i.e. in projecting down the $[10\bar{1}]$ direction. The structure amplitudes of planes in this zone are given by the expressions:

$$F_{hkh}=4\Sigma f_r\cos 2\pi(h+1)\,x_r\cos 2\pi k y_r \qquad k+h=2n,$$

$$F_{hkh}=-4\Sigma f_r\sin 2\pi(h+1)\,x_r\sin 2\pi k y_r \qquad k+h=2n+1,$$

where x_r is expressed as a fraction of half the (101) spacing.

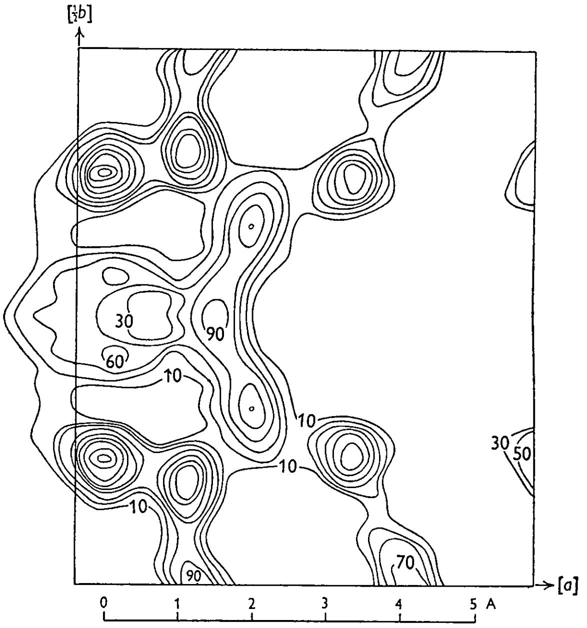


Fig. 2. Final projection on (001). Contours are drawn on an arbitrary scale. The 10-unit contour is indicated and other contours are drawn at equal intervals of 20 units, except in the case of the 60-unit contour marked.

Two sets of co-ordinates were obtained, both of which produced reasonable agreement between calculated and observed values of the structure amplitudes for the limited number of planes for which Bragg charts had been constructed; an attempt was then made to eliminate one of these sets of co-ordinates and to refine the other by a series of two-dimensional Fourier projections on to the $(10\bar{1})$ plane. Unfortunately, too much interference from the second molecule, derived from the first by the operation of the glide plane, made interpretation so difficult that this approach had to be abandoned, although sufficient evidence was secured to eliminate the first set of co-ordinates. From the second set of co-ordinates (x expressed as fraction of $\frac{1}{2}d_{101}$; y expressed as fraction of d_{010}) true x, y co-ordinates were calculated, and a series of two-dimensional Fourier projections on to the $c\,(001)$ face were computed; the earlier ones included only planes with $\xi<1{\cdot}00$, but eventually all the planes $\{hk0\}$ were incorporated. The final projection (Fig. 2) (in which the contours are drawn at arbitrary heights) shows poor resolution, but, nevertheless, a set of x, y co-ordinates can be obtained. From these x co-ordinates a set of z co-ordinates was calculated on the assumption that the molecule lay accurately in the $10\bar{2}$ plane, whence $x=2z$. These z co-ordinates were then refined by means of a series of two-dimensional Fourier projections on $a\,(100)$; the final projection is illustrated in Fig. 3.

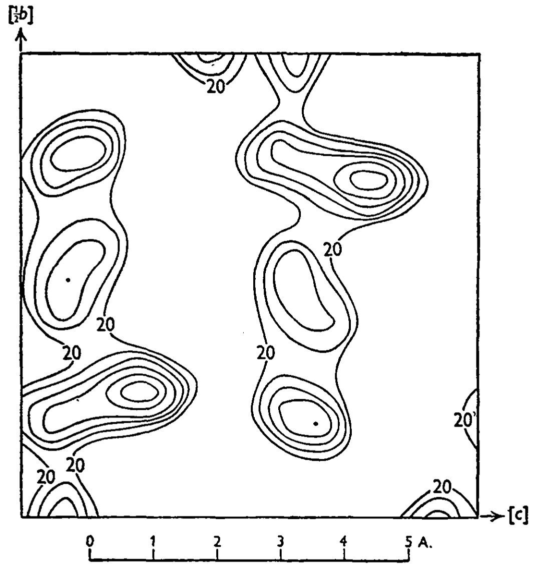


Fig. 3. Final projection on (100). Contours are drawn on an arbitrary scale. The 20-unit contour is indicated and other contours are drawn at equal intervals of 20 units.

Here again poor resolution vitiated the accuracy of the y, z co-ordinates, but it was obvious that the x co-ordinates were not, in general, twice the z co-ordinates. A sectional projection (Booth, 1945) did little to improve matters, and so we combined the co-ordinates from the two Fourier projections and the section-projection to produce a compromise set of x, y, z co-ordinates with which to commence systematic refinement by constructing three-dimensional Fourier lines and sections.

These co-ordinates, expressed as fractions of the axial length, are given in Table 1.

Two complete cycles of three-dimensional syntheses, involving a section and a line through each atom, indicated that the refinement of the co-ordinates by this method would be slow; the co-ordinates resulting from the second cycle demonstrated, however, that although the molecule was probably planar it did not lie exactly in the $10\bar{2}$ plane nor in any plane which passed through the origin.

Table 1. *Preliminary co-ordinates*

	x	y	z
C_2	0·247	0·067	0·128
C_3	0·387	0·153	0·180
C_4	0·356	0·329	0·180
C_5	0·227	0·406	0·160
C_6	0·047	0·385	0·065
C_7	−0·017	0·295	0·043
C_8	0·103	0·214	0·063
C_9	0·297	0·235	0·157
N	0·077	0·118	0·045
O_2	0·273	−0·017	0·107
O_3	0·537	0·138	0·303

In order to speed up the refinement of the co-ordinates a new approach was made based on the following argument. In the case of a structure with space-group symmetry $P2_1/c$ and in which the atoms are all located in the $10\bar{2}$ plane passing through the origin, i.e. in which $x=2z$, the normal form of the structure-amplitude equation, namely,

$$F_{hkl}=4\Sigma f[\cos 2\pi(hx+lz)\cos 2\pi ky\cos^2 2\pi(k+l)/4 \\ -\sin 2\pi(hx+lz)\sin 2\pi ky\sin^2 2\pi(k+l)/4],$$

can be written

$$F_{hkl}=4\Sigma f\cos 2\pi(2h+l)z\cos 2\pi ky \quad k+l=2n,$$

$$F_{hkl}=-4\Sigma f\sin 2\pi(2h+l)z\sin 2\pi ky \quad k+l=2n+1.$$

Then the planes hkl for which $(2h+l)$ and k are constant will differ from one another only in the values which are assigned to the atomic scattering factors; their phases will all be the same. For isatin the relationship $x=2z$ is not accurately true, but, nevertheless, it is to be expected that the phase relationship will hold approximately and will be of considerable value in assigning a phase to many of the $\{hkl\}$ structure amplitudes. The planes with $(h+2l)$ and k constant are easily obtained from the a^*c^* reciprocal net, since they lie in straight lines parallel to the 201 direction. This arrangement of the structure amplitudes of all the planes up to a ρ value of 1·2 indicated that, in all but twenty-five cases, the phases (as calculated from the co-ordinates so far determined) remained constant. A portion of the table of structure amplitudes (together with the phase calculated from the final atomic co-ordinates) is reproduced in Table 2. This table includes all the planes for which $2h+l=2$, and those in each column satisfy the conditions $(2h+l)$ and k constant. Omitting those structure amplitudes whose calculated

Table 2. *Portion of table of structure amplitudes arranged for the computation of section parallel to* $(10\bar{2})$

hl \ k	0	1	2	3	4	5	6	7	8	9	10	11
$\bar{3}8$	—	− 8·2	—	—	—	—	—	—	—	—	—	—
$\bar{2}6$	−2·0	−19·2	—	—	—	3·4	—	7·0	—	—	—	—
$\bar{1}4$	−3·8	−49·0	—	− 7·7	6·0	6·8	—	13·8	—	—	—	−5·1
02	−3·4	−58·0	− 6·4	−10·0	12·7	9·8	− 9·5	17·6	—	7·4	—	−4·7
10	3·0	−55·0	−11·6	− 4·3	7·0	3·2	−19·0	10·8	1·8	13·8	4·0	4·2
$2\bar{2}$	4·1	− 4·9	− 3·4	3·1	−8·1	−4·3	−11·0	—	5·8	11·4	6·3	6·7
$3\bar{4}$	3·0	—	—	—	−7·4	−5·0	− 5·1	—	2·7	5·3	4·0	3·9
$4\bar{6}$	—	—	—	—	—	—	—	—	—	—	—	—

phase is at variance with the pattern, a three-dimensional section passing through the origin and lying in the $10\overline{2}$ plane was computed, using the summation

$$\rho_{xyz}=\frac{4}{V}\sum_{2h+l=0}^{2H+L}\sum_{0}^{K}\begin{bmatrix}F_{hkl}\\ 2h+l=\text{const.}\\ k+l=2n\end{bmatrix}\cos 2\pi(2h+l)z\cos 2\pi ky$$

$$-\frac{4}{V}\sum_{2h+l=0}^{2H+L}\sum_{0}^{K}\begin{bmatrix}F_{hkl}\\ 2h+l=\text{const.}\\ k+l=2n+1\end{bmatrix}\sin 2\pi(2h+l)z\sin 2\pi ky.$$

In computing this summation care was taken in the arrangement of terms such that $2h+l>0$, and in the multiplicity corrections to be applied to F_{0k0} and F_{h0l}.

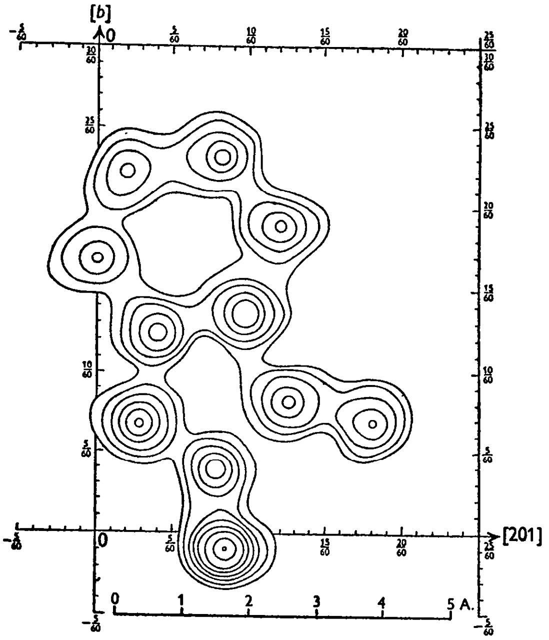


Fig. 4. Final electron-density map of section parallel to $(10\overline{2})$ and passing through the origin.

The final electron-density map of the section parallel to $(10\overline{2})$ and passing through the origin, obtained using all the structure amplitudes, is shown in Fig. 4. When one remembers that the isatin molecule does not lie accurately in the $10\overline{2}$ plane (the plane of the molecule is actually some 10° from $10\overline{2}$), it is remarkable that the phases of the structure amplitudes F_{hkl}, for which $2h+l$ and k are constant, remain unaltered except when the function obviously passes through zero with changing values of h and l. Although it is not possible to formulate an exact treatment of such a case it is possible to state it in general terms. If a mean crystallographic plane of low indices, passing through the origin, is drawn through the flat or approximately flat molecule, then on arranging the structure amplitudes in columns in the zone of the corresponding axis, the magnitude of F_{hkl} will bear out a wave-like function of low frequency with changing h and l and the phases will remain constant excepting where values of F_{hkl} appear to pass through zero.

Following these $(10\overline{2})$ sections the structure was quickly refined by a series of three-dimensional sections parallel to the a, c plane and a series of three-dimensional lines parallel to $[b]$. The final co-ordinates are given in Table 3.

Table 3. *Final co-ordinates*

	x	y	z
C_2	0·262	0·065	0·130
C_3	0·431	0·135	0·187
C_4	0·399	0·314	0·184
C_5	0·259	0·385	0·135
C_6	0·047	$0{\cdot}366_5$	0·065
C_7	−0·024	0·277	0·038
C_8	0·119	0·208	0·085
C_9	0·328	0·226	0·155
N	0·085	0·114	0·069
O_2	0·280	−0·018	0·135
O_3	0·612	0·118	0·249

In calculating the structure amplitudes from these co-ordinates we have assumed that the contributions of carbon, nitrogen and oxygen atoms are in the ratio 1 : 1·17 : 1·33, and the most satisfactory atomic scattering factor curve for carbon in this compound has been determined from the equation

$$f_c=F_{hkl,\text{obs.}}/F'_{hkl,\text{calc.}},\quad \text{where}\quad F'_{\text{calc.}}=\phi(hkl)(x,y,z).$$

Values of the atomic scattering factor for carbon in isatin for various values of $\rho=2\sin\theta$ are listed in Table 4.

Table 4. *Variation in atomic scattering factor with ρ for a carbon atom in isatin*

ρ	0·1	0·2	0·3	0·4	0·5	0·6
f_c	5·78	5·25	4·68	4·13	3·58	3·19
ρ	0·7	0·8	0·9	1·0	1·1	1·2
f_c	2·64	2·20	1·83	1·50	1·23	1·02
ρ	1·3	1·4	1·5	1·6	1·7	1·8
f_c	0·85	0·70	0·56	0·45	0·38	0·33

The structure amplitudes calculated from the final co-ordinates, together with the observed values, are listed in Table 8. The average discrepancy, calculated from the expression

$$R_1=\frac{\Sigma\,||F_{\text{obs.}}|-|F_{\text{calc.}}||}{\Sigma\,|F_{\text{obs.}}|},$$

is 0·20.

Using the expression

$$R_2=\frac{hkl\,||F_{\text{obs.}}|-|F_{\text{calc.}}||^2}{hkl\,|F_{\text{obs.}}|^2},$$

where F_{000}, F_{0k0}, etc., have been corrected for their multiplicity, leads to $R_2=0{\cdot}054$. This second value (R_2) is useful in that it is related to the root mean square error in the atomic co-ordinates, giving a value for this quantity of 0·018 A.

Discussion of the structure

The bond lengths and angles calculable from the final set of atomic co-ordinates are given in Table 5.

All distances between atoms in neighbouring molecules, other than the $N\cdots H\cdots O_2$ distance, were found to be greater than the required minimum distance for non-bonded atoms. The plane of the molecule makes an angle of 9° with $(10\bar{2})$ and 1° with $[b]$; the plane does not pass through the origin of the unit cell. The two associated molecules do not lie in the same plane, and as a result the hydrogen bond lies out of the plane of the molecules.

Table 5. *Bond lengths and angles*

C_2–C_3	1·49 A.	C_6–C_7	1·37 A.
C_3–C_9	1·47 A.	C_8–C_7	1·36 A.
C_9–C_8	1·37 A.	N–C_8	1·38 A.
C_9–C_4	1·36 A.	N–C_2	1·35 A.
C_4–C_5	1·37 A.	C_2–O_2	1·21 A.
C_5–C_6	1·39 A.	C_3–O_3	1·19 A.

N···H···O_2 2·93 A.

Six-membered ring		Five-membered ring	
C_6–C_7–C_8	118°	C_8–N–C_2	112°
C_7–C_8–C_9	122°	N–C_2–C_3	105°
C_8–C_9–C_5	121°	C_2–C_3–C_9	105°
C_9–C_4–C_5	118°	C_3–C_9–C_8	106°
C_4–C_5–C_6	120°	C_9–C_8–N	111°
C_5–C_6–C_7	121°		

External angles

C_7–C_8–N	128°	C_2–C_3–O_3	125°
N–C_2–O_2	127°	O_3–C_3–C_9	129°
O_2–C_2–C_3	127°	C_3–C_9–C_4	133°

The separation N···H···O_2 = 2·93 A. and the bond length C_2–O_2 = 1·21 A. suggest strongly the preponderance of resonance contributors in which the –NH grouping persists, and appear to rule out the probability of this hydrogen atom being situated midway between N^- and O_2. The most probable resonance contributors are illustrated in Fig. 5, their contributions to the structure being determined experimentally by the use of Pauling's equation

$$R=\frac{x_1k_1R_1+x_2k_2R_2}{x_1k_1+x_2k_2},$$

where R_1 and R_2 are single- and double-bond lengths, x_1 and x_2 are the degree of single- and double-bond character in a bond, and k_1 and k_2 are the force constants for single and double bonds.

In the calculations we used the lengths of single bonds, double bonds and bonds where one atom carries a formal charge as shown in Table 6.

Table 6. *Lengths of bonds*

	C–C	C–N	C–O
Single	1·54 A.	1·47 A.	1·43 A.
Double	1·33 A.	1·26 A.	1·21 A.
Single^-	1·56 A.	—	1·45 A.
Single^+	—	1·45 A.	—
Double^+	—	1·23 A.	—
Single^+ incomplete	1·43 A.	—	—

The large number of probable resonance contributors makes the assessment of their individual contribution to the whole structure a difficult task, and consequently the various weights which have been allotted are not expected to be accurate; nevertheless, they indicate quite clearly and unequivocally the general pattern. The weighting of each contributor has been assessed by consideration of the observed bond distances C_2–O_2 = 1·21, C_3–O_3 = 1·19, C_2–N = 1·35, C_8–N = 1·38, C_9–C_3 = 1·47 A., in the following manner.

The usually accepted value for C=O is 1·21 A., which is 0·02 A. longer than the bond C_3–O_3 and equal to the bond C_2–O_2. The discrepancy in these latter observed distances can be explained by assuming that the single-bond character of C_2–O_2 exceeds that of C_3–O_3 by some 15–20 %. The shortness of C_3–O_3 must mean that this bond is almost, if not completely, double bond in character and that the value of 1·21 A. for such a bond needs some revision. It is obvious, however, that those resonance contributors involving single-bond character for either or both bonds C_2–O_2 and C_3–O_3 play only a limited part, and that therefore the lactam form of the molecule predominates over the lactim form. C_2–N and C_8–N have approximately 30 and 20 % double-bond character; on writing down such contributors, however, we find that inevitably the single-bond character of either or both the bonds C_2–O_2 and C_3–O_3 must be increased. Further, in permitting some 10 % double-bond character in the bond C_9–C_3 we must again increase the single-bond character of C_3–O_3.

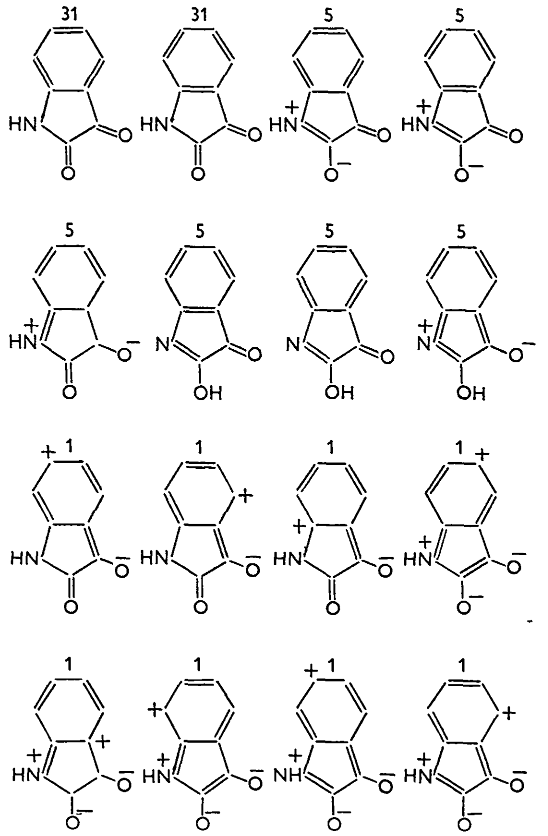


Fig. 5. Resonance contributors. The number above each hybrid indicates its percentage contribution to the structure.

Considerations such as these place very severe restrictions on the choice of weights for the resonance contributors and lead in general to calculated bond lengths which are greater than the observed values. In Fig. 5 the thirteen most probable variants on the classical lactam molecule together with the three lactim hybrids are illustrated. There is no question that all these contribute in greater or less degree, and it is probable that other forms of the molecule which are even less stable also play some part. The lactim variants contribute approximately 15 % to the total structure, and therefore the hydrogen nucleus is more closely associated with the nitrogen atoms in the molecule-pair than with the oxygen atoms. The intra-molecular separation of these two atoms (2·93 A.), and the fact that the line joining them lies out of the plane of the molecule, indicate that the hydrogen bonding is not strong and suggest unequal sharing of the hydrogen atom.

Within the benzene ring each C–C bond has approximately 50 % single-bond character, 1–3 % single-bond character in which one carbon atom has an incomplete shell of electrons, and 46–49 % double-bond character. The participation of the resonance forms in which a carbon atom carries a positive charge probably accounts for the smallness of the benzene ring; the irregularity of the ring arises partly from the non-equivalence of the bonds but mainly from the strain set up by the adjoining five-membered heterogeneous ring. Longuet-Higgins & Coulson (1946) have calculated the appropriate corrections arising from this cause to be

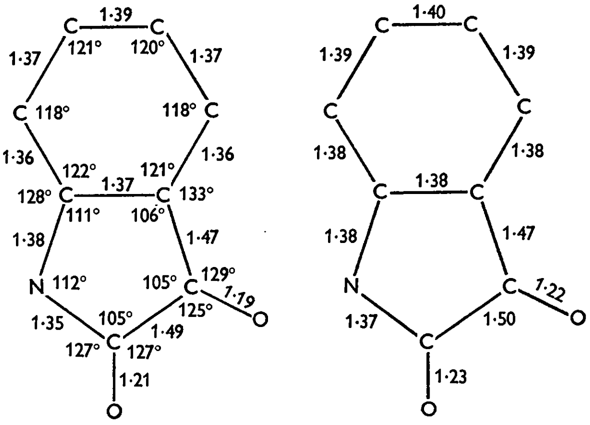
$$\begin{aligned} C_9\text{–}C_8 &= -0{\cdot}02\,\text{A.}, \\ C_8\text{–}C_7 \text{ and } C_9\text{–}C_4 &= -0{\cdot}004\,\text{A.}, \\ C_7\text{–}C_6 \text{ and } C_5\text{–}C_4 &= +0{\cdot}004\,\text{A.}, \\ C_6\text{–}C_5 &= +0{\cdot}02\,\text{A.} \end{aligned}$$

Only the first and last of these has any real significance, and result in closer approximation of the theoretical bond lengths to those actually observed. The calculated interatomic distances, in which the resonance hybrids are accorded the weights shown in Fig. 5, are listed in Table 7, and the theoretical molecule is illustrated alongside the experimental one in Fig. 6.

Table 7. *Calculated interatomic distances*

C_2–C_3	1·50 A.	C_6–C_5	1·40 A.	N–C_8	1·39 A.
C_3–C_9	1·47 A.	C_4–C_5	1·37 A.	N–C_2	1·34 A.
C_9–C_8	1·39 A.	C_6–C_7	1·37 A.	C_2–O_2	1·24 A.
C_9–C_4	$1{\cdot}37_6$ A.	C_8–C_7	$1{\cdot}37_6$ A.	C_3–O_3	1·23 A.

The greatest discrepancy between the observed and calculated bond distances (0·03 A.) occurs in the C_3–O_3 bond; apart from this, however, the agreement is good enough to justify the conclusion that the lactam form of the molecule predominates in the structure and that the resonance forms illustrated in Fig. 5 contribute approximately in the proportions indicated. In these circumstances it is reasonable to suppose that the addition of substituents to the isatin molecule will produce stable derivatives only when the bond distribution necessitated by the lactam configuration is adhered to reasonably closely. Thus the N-ether will be more stable than the O-ether, and further the decomposition of the relatively unstable O-ether will occur in such a manner as to reproduce the lactam conditions as nearly as possible.



Experimental Theoretical

Fig. 6. Bond lengths and angles.

A feature of the section in the 10$\bar{2}$ plane which is of interest is the apparent decrease in the value of the electron-density maxima with increasing distance from the origin. A similar effect has been commented on by G. A. Jeffrey, who found that in geranylamine hydrochloride the electron-density maxima decreased in magnitude with increasing distance from the chloride ion. A probable explanation, at least in the case of isatin, is that thermal agitation of the atoms is greater at the benzenoid end of the molecule, where the intra-molecular forces are least.

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Table 8. *Observed and calculated structure factors*

$k+l=2n$

Plane	$F_{\text{obs.}}$	$F_{\text{calc.}}$
020	22·5	−26·8
040	31·5	−34·5
060	10·0	− 8·5
080	33·6	30·2
0,10,0	15·0	12·3
0,12,0	20·0	−18·6
0,14,0	<2·3	2·6
0,16,0	3·6	3·3
100	6·1	2·4
120	11·6	−14·0
140	7·0	8·6
160	19·0	−13·3
180	1·8	2·5
1,10,0	4·0	1·2
1,12,0	3·7	− 2·9
1,14,0	3·7	2·6
1,16,0	2·8	− 2·1
200	<1·1	− 1·9
220	36·0	−37·5
240	30·0	−21·2
260	<1·7	3·3
280	4·5	6·2
2,10,0	<2·2	− 2·6
2,12,0	5·0	− 4·1
2,14,0	<2·2	1·0
300	33·5	33·0
320	2·4	− 5·8
340	2·9	5·7
360	3·5	− 4·3
380	8·3	8·4
3,10,0	<2·3	0·3
3,12,0	<2·4	− 1·6
3,14,0	1·9	0·4
400	<2·0	− 0·5
420	14·5	14·5
440	8·7	7·8
460	<2·2	− 2·1
480	<2·4	1·9
4,10,0	4·1	− 4·6
4,12,0	<2·2	2·9
500	<2·3	− 1·9
520	4·5	− 5·4
540	6·7	− 6·3
560	<2·4	1·7
580	<2·4	− 0·4
5,10,0	<2·1	− 1·7
600	10·4	−10·2
620	4·8	− 4·6
640	8·1	8·3
660	<2·1	− 1·0
680	<2·1	− 1·7
700	2·7	3·0
720	<1·9	0·4
740	<1·8	2·1
011	20·8	27·1
031	21·0	25·0
051	6·4	7·5
071	4·4	− 7·1
091	5·1	3·8
0,11,1	<2·3	2·0
0,13,1	<2·4	− 0·2
0,15,1	<2·2	0·8
111	12·4	−10·5
131	23·0	−23·4
151	32·4	−26·2
171	3·8	5·2
191	<2·0	− 1·9
1,11,1	15·5	14·1
1,13,1	17·0	−13·9
1,15,1	<2·2	− 1·0
211	23·5	−23·7
231	10·4	10·1
251	11·4	−14·7
271	10·0	9·4
291	5·2	− 3·8
2,11,1	<2·3	− 1·1
2,13,1	<2·4	1·6
2,15,1	<2·0	− 0·6
311	13·4	7·2
331	21·5	21·0
351	6·0	6·6
371	<2·0	− 0·4
391	4·0	− 6·9
3,11,1	5·9	6·5
3,13,1	<2·3	0·2
3,15,1	<1·8	− 0·6
411	4·3	− 6·4
431	10·5	11·2
451	6·4	− 6·1
471	7·4	8·5
491	11·2	−12·5
4,11,1	<2·2	0·6
4,13,1	<2·0	1·0
511	17·4	−11·8
531	<2·3	0·2
551	3·0	− 3·1
571	<2·4	1·0
591	4·0	− 2·3
611	3·7	2·7
631	3·6	− 3·3
651	<2·2	1·4
671	<2·0	1·7
711	<2·3	0·2
731	3·6	4·1
002	6·8	−10·3
022	6·4	−11·2
042	12·4	15·5
062	9·5	− 8·9
082	<1·9	− 1·7
0,10,2	<2·2	0·0
0,12,2	<2·3	− 0·7
0,14,2	3·3	2·5
0,16,2	3·4	− 2·8
102	7·7	−15·6
122	25·0	−32·2
142	22·7	−21·5
162	1·7	1·0
182	6·4	6·4
1,10,2	<2·1	− 2·6
1,12,2	4·5	− 3·5
1,14,2	<2·2	− 0·3
1,16,2	<1·9	0·1
202	21·6	24·3
222	4·1	−10·1
242	13·8	14·8
262	<1·9	− 0·2
282	2·6	2·5
2,10,2	<2·3	− 3·2
2,12,2	<2·4	1·0
2,14,2	3·9	1·2
2,16,2	<1·8	− 1·0
302	2·2	− 3·3
322	16·5	14·3
342	13·5	12·9
362	2·6	− 4·6
382	<2·3	0·5
3,10,2	4·5	− 3·8
3,12,2	4·0	3·1
3,14,2	<2·1	1·9
402	<2·2	− 2·2
422	7·4	− 7·4
442	6·9	− 5·0
462	<2·3	2·1
482	<2·4	− 1·4
4,10,2	<2·3	− 2·1
4,12,2	<2·0	0·0
502	15·0	−15·1
522	8·4	− 9·0
542	15·5	14·8
562	<2·4	− 1·8
582	6·7	− 4·5
5,10,2	<2·0	− 1·3
602	6·8	6·8
622	<2·2	0·4
642	2·7	2·1
662	<2·0	0·6
682	<1·8	0·7
702	<2·0	2·9
013	14·0	−19·5
033	6·4	− 9·7
053	12·0	−11·0
073	<2·0	2·6
093	7·0	− 5·1
0,11,3	12·3	11·1
0,13,3	9·7	− 8·6
0,15,3	<2·2	− 1·3
113	19·4	−16·8
133	3·8	4·5
153	17·5	−14·4
173	12·8	10·9
193	3·5	− 3·4
1,11,3	3·8	− 2·8
1,13,3	<2·3	1·8
1,15,3	<2·0	− 1·2
213	9·5	8·7
233	15·3	16·5
253	3·4	5·5
273	3·4	2·2
293	4·7	− 5·9
2,11,3	4·1	3·3
2,13,3	<2·2	0·8
313	6·1	− 5·3
333	11·6	10·7
353	<2·2	− 1·7
373	6·9	7·5
393	14·0	−13·4
3,11,3	<2·3	2·2
413	9·9	− 7·7
433	<2·3	− 4·1
453	5·9	− 7·6
473	3·0	4·2
493	<2·2	0·0
4,11,3	<1·9	− 1·1

Table 8 (*cont.*)

$k+l=2n$ (*cont.*)

Plane	$F_{\text{obs.}}$	$F_{\text{calc.}}$
513	< 2·4	2·4
533	3·4	− 3·4
553	2·8	2·6
573	< 2·2	1·3
593	< 1·9	2·1
613	< 2·1	1·7
633	4·2	4·0
653	< 1·9	1·0
673	< 1·7	2·1
004	16·2	−21·9
024	7·7	−10·0
044	8·3	−10·4
064	< 2·1	− 0·8
084	3·1	2·6
0,10,4	< 2·3	− 2·0
0,12,4	< 2·3	− 0·6
0,14,4	2·5	− 1·8
104	3·8	4·0
124	3·8	− 5·0
144	12·6	14·1
164	< 2·1	1·4
184	3·2	− 3·0
1,10,4	3·8	− 3·5
1,12,4	3·6	3·4
204	< 2·0	− 2·5
224	13·8	13·5
244	9·9	10·0
264	4·5	− 5·3
284	< 2·4	0·6
2,10,4	< 2·4	− 1·6
2,12,4	2·7	2·6
304	4·5	− 5·5
324	5·6	− 6·4
344	< 2·3	− 1·1
364	< 2·4	2·3
384	4·1	− 4·2
3,10,4	< 2·3	− 1·6
404	14·0	−13·5
424	8·8	− 9·3
444	15·0	14·8
464	< 2·3	− 2·1
484	*	− 5·3
504	9·4	8·2
524	< 2·3	0·1
544	< 2·2	1·6
564	< 2·0	− 0·6
604	< 1·9	3·0
015	3·9	− 5·3
035	< 2·1	− 1·3
055	7·7	− 9·5
075	7·4	8·2
095	< 2·6	− 0·8
0,11,5	2·8	− 3·7
0,13,5	< 1·9	0·5
115	3·8	4·5
135	8·1	9·1
155	3·6	5·5
175	< 2·3	1·0
195	3·8	− 4·5
1,11,5	< 2·2	0·5
215	< 2·2	− 3·7
235	5·6	6·8
255	3·7	1·2
275	5·4	3·7
295	5·1	− 9·9
315	3·8	− 3·3
335	4·8	− 6·5
355	5·3	− 7·9
375	3·3	3·8
395	3·8	2·4
415	< 2·4	1·0
435	< 2·4	− 2·5
455	< 2·1	4·2
475	< 2·0	− 0·6
495	< 1·8	0·2
515	2·6	3·3
535	< 2·2	2·3
555	< 2·2	0·0
575	< 2·2	2·3
595	< 1·9	− 2·1
006	< 2·3	− 1·8
026	< 2·3	− 1·3
046	5·5	7·6
066	< 2·4	1·7
086	2·3	− 3·5
0,10,6	< 2·3	− 2·5
106	3·4	− 1·4
126	7·3	9·1
146	4·5	5·1
166	3·8	− 3·5
186	< 2·3	0·4
206	4·8	− 6·7
226	< 2·4	− 4·1
246	< 2·4	0·9
266	2·0	2·5
286	< 2·3	4·0
306	6·0	− 8·2
326	4·7	− 6·6
346	6·7	7·9
366	< 2·1	− 1·8
406	6·0	7·3
426	< 2·0	0·6
446	< 2·0	0·6
017	< 2·3	1·7
037	4·4	4·0
057	< 2·2	4·0
117	< 2·3	− 0·7
137	< 2·3	1·5
157	< 2·2	1·6
217	< 2·2	− 0·5
237	2·7	− 5·3
257	3·9	− 5·3
317	< 2·0	− 0·1
337	< 1·9	− 2·1
357	3·6	4·8
417	2·4	4·0
008	< 1·9	− 0·8
$11\bar{1}$	6·3	9·7
$13\bar{1}$	25·0	26·0
$15\bar{1}$	17·2	18·6
$17\bar{1}$	15·5	−14·5
$19\bar{1}$	< 2·0	− 2·9
$1,11,\bar{1}$	6·7	4·7
$1,13,\bar{1}$	< 2·4	1·0
$1,15,\bar{1}$	< 2·2	0·5
$21\bar{1}$	7·2	− 6·8
$23\bar{1}$	29·0	−28·9
$25\bar{1}$	29·5	−25·0
$27\bar{1}$	2·4	3·6
$29\bar{1}$	5·1	3·3
$2,11,\bar{1}$	11·8	10·5
$2,13,\bar{1}$	17·0	−13·0
$31\bar{1}$	10·3	−14·2
$33\bar{1}$	2·9	6·8
$35\bar{1}$	8·3	− 8·8
$37\bar{1}$	4·1	3·8
$39\bar{1}$	2·8	− 0·6
$3,11,\bar{1}$	< 2·4	− 0·8
$3,13,\bar{1}$	< 2·1	0·8
$41\bar{1}$	5·3	3·9
$43\bar{1}$	15·5	15·0
$45\bar{1}$	7·5	9·0
$47\bar{1}$	2·8	− 3·1
$49\bar{1}$	3·4	− 5·0
$4,11,\bar{1}$	6·7	5·4
$4,13,\bar{1}$	< 2·0	1·0
$51\bar{1}$	< 2·3	− 2·0
$53\bar{1}$	4·6	6·3
$55\bar{1}$	7·9	− 6·9
$57\bar{1}$	6·2	5·7
$59\bar{1}$	5·0	− 6·0
$5,11,\bar{1}$	< 1·9	0·6
$61\bar{1}$	9·7	− 9·0
$63\bar{1}$	3·7	1·9
$65\bar{1}$	< 2·2	− 0·1
$67\bar{1}$	< 2·2	− 1·1
$71\bar{1}$	< 1·9	1·7
$73\bar{1}$	< 1·9	− 2·2
$10\bar{2}$	110·0	162·0
$12\bar{2}$	9·4	−15·0
$14\bar{2}$	15·0	−21·4
$16\bar{2}$	4·8	− 5·6
$18\bar{2}$	18·0	18·0
$1,10,\bar{2}$	11·0	8·0
$1,12,\bar{2}$	14·6	−12·7
$1,14,\bar{2}$	< 2·2	1·5
$1,16,\bar{2}$	2·7	2·9
$20\bar{2}$	8·2	7·9
$22\bar{2}$	3·4	− 5·1
$24\bar{2}$	8·1	− 4·3
$26\bar{2}$	11·0	−12·8
$28\bar{2}$	5·8	5·8
$2,10,\bar{2}$	6·3	3·3
$2,11,\bar{2}$	6·1	− 4·5
$2,14,\bar{2}$	< 2·2	1·2
$30\bar{2}$	< 2·1	− 2·0
$32\bar{2}$	19·0	−23·0
$34\bar{2}$	14·7	−10·4
$36\bar{2}$	5·0	4·2
$38\bar{2}$	< 2·2	− 1·6
$3,10,\bar{2}$	< 2·3	− 1·1

* Not observed because plane lies in such a position on the limiting sphere that only photograph in the [111] zone would give its intensity.

Table 8 (*cont.*)

$k+l=2n$ (*cont.*)

Plane	$F_{\text{obs.}}$	$F_{\text{calc.}}$
$3,12,\bar{2}$	3·7	−2·9
$3,14,\bar{2}$	<2·2	1·3
$40\bar{2}$	21·5	20·8
$42\bar{2}$	<2·1	−1·1
$44\bar{2}$	<2·2	−1·4
$46\bar{2}$	<2·3	−3·8
$48\bar{2}$	6·7	7·1
$4,10,\bar{2}$	<2·3	1·6
$4,12,\bar{2}$	2·6	−2·8
$50\bar{2}$	<2·3	2·4
$52\bar{2}$	10·0	9·3
$54\bar{2}$	<2·3	−0·9
$56\bar{2}$	<2·4	−0·7
$58\bar{2}$	<2·3	2·0
$5,10,\bar{2}$	2·9	−2·7
$60\bar{2}$	4·6	−3·2
$62\bar{2}$	<2·3	−1·9
$64\bar{2}$	4·0	−4·1
$66\bar{2}$	3·1	1·6
$68\bar{2}$	<2·0	−0·6
$70\bar{2}$	3·9	−5·8
$72\bar{2}$	<1·9	−2·1
$11\bar{3}$	18·4	26·0
$13\bar{3}$	4·5	3·1
$15\bar{3}$	2·2	−1·8
$17\bar{3}$	<1·9	0·5
$19\bar{3}$	6·7	5·5
$1,11,\bar{3}$	3·4	−2·2
$1,13,\bar{3}$	<2·2	−0·2
$1,15,\bar{3}$	<1·9	1·3
$21\bar{3}$	2·1	0·9
$23\bar{3}$	11·2	15·6
$25\bar{3}$	14·7	16·4
$27\bar{3}$	12·4	−12·7
$29\bar{3}$	<2·3	−2·6
$2,11,\bar{3}$	4·1	4·0
$2,13,\bar{3}$	2·3	2·2
$31\bar{3}$	<1·9	−0·3
$33\bar{3}$	14·8	−15·4
$35\bar{3}$	11·2	−12·0
$37\bar{3}$	<2·2	0·7
$39\bar{3}$	4·8	4·3
$3,11,\bar{3}$	4·8	4·8
$3,13,\bar{3}$	6·7	−8·0
$41\bar{3}$	<2·0	−2·3
$43\bar{3}$	<2·3	−0·5
$45\bar{3}$	3·2	−5·2
$47\bar{3}$	<2·3	−0·4
$49\bar{3}$	5·3	4·4
$4,11,\bar{3}$	<2·3	−0·9
$51\bar{3}$	<2·3	1·2
$53\bar{3}$	6·3	8·0
$55\bar{3}$	4·8	7·5
$57\bar{3}$	2·9	−4·3
$59\bar{3}$	<2·0	−2·8
$5,11,\bar{3}$	2·2	3·8
$61\bar{3}$	<2·1	−0·2
$63\bar{3}$	<2·1	2·2
$65\bar{3}$	4·0	−4·0
$67\bar{3}$	2·4	2·7
$10\bar{4}$	7·5	−10·5
$12\bar{4}$	<2·1	−1·0
$14\bar{4}$	6·0	7·4
$16\bar{4}$	<2·1	−2·1
$18\bar{4}$	<2·3	−2·5
$1,10,\bar{4}$	<2·4	−1·0
$1,12,\bar{4}$	<2·3	0·9
$1,14,\bar{4}$	<2·0	1·3
$20\bar{4}$	47·0	53·0
$22\bar{4}$	5·1	−3·0
$24\bar{4}$	5·1	−4·5
$26\bar{4}$	<2·3	−0·4
$28\bar{4}$	4·7	5·9
$2,10,\bar{4}$	7·2	4·0
$2,12,\bar{4}$	5·6	−5·3
$2,14,\bar{4}$	<2·0	1·0
$30\bar{4}$	3·0	3·8
$32\bar{4}$	<2·1	0·8
$34\bar{4}$	7·4	−7·9
$36\bar{4}$	5·1	−6·2
$38\bar{4}$	2·7	4·2
$3,10,\bar{4}$	4·0	3·1
$3,12,\bar{4}$	<2·0	−3·5
$40\bar{4}$	<2·3	−1·9
$42\bar{4}$	7·2	−9·1
$44\bar{4}$	4·4	−5·9
$46\bar{4}$	<2·4	4·1
$48\bar{4}$	*	−4·0
$50\bar{4}$	6·2	9·3
$52\bar{4}$	<2·4	0·9
$54\bar{4}$	<2·4	−1·6
$56\bar{4}$	<2·3	−1·8
$60\bar{4}$	<2·1	3·1
$62\bar{4}$	4·3	4·9
$64\bar{4}$	<2·1	−3·5
$11\bar{5}$	7·9	−11·4
$13\bar{5}$	<2·2	−2·2
$15\bar{5}$	3·1	−1·8
$17\bar{5}$	<2·3	−0·2
$19\bar{5}$	5·1	−5·1
$1,11,\bar{5}$	5·8	5·8
$1,13,\bar{5}$	3·5	−3·4
$21\bar{5}$	8·4	11·9
$23\bar{5}$	<2·2	−0·3
$25\bar{5}$	<2·2	−2·3
$27\bar{5}$	<2·3	1·8
$29\bar{5}$	3·7	5·0
$2,11,\bar{5}$	4·9	−3·8
$31\bar{5}$	<2·3	0·7
$33\bar{5}$	<2·3	4·8
$35\bar{5}$	8·0	8·9
$37\bar{5}$	3·4	−7·9
$39\bar{5}$	<1·9	−1·1
$41\bar{5}$	<2·4	−0·8
$43\bar{5}$	5·4	−8·5
$45\bar{5}$	<2·4	−3·7
$47\bar{5}$	<2·2	−0·5
$51\bar{5}$	<2·3	0·5
$53\bar{5}$	<1·8	−2·2
$55\bar{5}$	<2·1	−1·9
$59\bar{5}$	*	5·5
$10\bar{6}$	16·5	−19·5
$12\bar{6}$	<2·3	−1·8
$14\bar{6}$	<2·3	−1·9
$16\bar{6}$	<2·4	−0·1
$18\bar{6}$	<2·2	−1·7
$1,10,\bar{6}$	<2·2	−1·5
$20\bar{6}$	4·1	−5·2
$22\bar{6}$	<2·4	1·3
$24\bar{6}$	<2·4	1·2
$26\bar{6}$	<2·3	−0·2
$28\bar{6}$	<2·2	−0·6
$30\bar{6}$	9·9	13·6
$32\bar{6}$	<1·9	0·8
$34\bar{6}$	<1·8	1·2
$40\bar{6}$	<2·9	0·6
$42\bar{6}$	<2·9	0·8
$44\bar{6}$	*	−3·2
$50\bar{6}$	<2·0	−1·4
$11\bar{7}$	<2·3	−1·4
$13\bar{7}$	<2·3	−2·2
$15\bar{7}$	2·3	−4·0
$17\bar{7}$	3·7	3·7
$21\bar{7}$	2·8	−5·1
$31\bar{7}$	*	3·5
$20\bar{8}$	8·8	−10·0

$k+l=2n-1$

Plane	$F_{\text{obs.}}$	$F_{\text{calc.}}$
110	55·0	−61·0
130	4·3	−4·8
150	3·2	3·0
170	10·8	11·6
190	13·8	11·5
1,11,0	4·2	2·2
1,13,0	11·0	8·0
1,15,0	3·8	2·6
210	4·8	−4·5
230	35·0	−29·5
250	12·0	8·0
270	13·8	13·7
290	4·0	−3·6
2,11,0	16·2	−12·0
2,13,0	<2·4	0·4
2,15,0	<2·0	1·3
310	12·8	−13·8
330	7·9	6·2
350	12·5	12·6
370	13·0	−10·6
390	5·1	−4·4
3,11,0	8·1	−6·0
3,13,0	<2·2	−1·2
410	7·5	−6·0
430	4·2	−5·7
450	2·2	1·6
470	9·0	8·3
490	<2·4	0·5
4,11,0	<2·2	−1·5
4,13,0	<2·0	2·4

Table 8 (*cont.*)

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

Plane	$F_{\text{obs.}}$	$F_{\text{calc.}}$
510	3·8	−3·8
530	16·7	−16·7
550	10·0	9·5
570	5·8	5·5
590	<2·2	−1·8
610	4·5	3·7
630	<2·3	−0·8
650	<2·2	0·9
670	2·4	−3·5
690	<1·7	−1·4
710	<1·9	1·7
730	<1·9	−0·6
750	<1·9	1·6
121	11·5	12·4
141	13·2	8·0
161	40·0	−32·0
181	14·8	13·0
1,10,1	16·0	13·2
1,12,1	<2·3	0·3
1,14,1	2·8	0·6
1,16,1	<2·0	0·8
221	22·5	−20·5
241	3·8	−2·8
261	6·7	9·0
281	<2·0	0·8
2,10,1	14·0	−10·0
2,12,1	16·0	−12·6
2,14,1	<2·1	0·5
321	11·4	−8·9
341	<1·9	0·0
361	6·0	4·1
381	11·0	10·4
3,10,1	11·3	−9·7
3,12,1	<2·4	−2·3
3,14,1	<2·0	−1·0
421	10·0	10·6
441	2·6	2·1
461	10·4	−13·2
481	3·8	4·4
4,10,1	9·5	10·8
4,12,1	5·5	2·3
4,14,1	<1·8	−1·0
521	<2·3	0·6
541	8·3	−7·5
561	7·1	5·2
581	2·8	−2·1
5,10,1	<1·8	−0·3
621	5·0	4·4
641	<2·2	0·5
661	4·0	−3·9
681	<2·0	−0·4
721	3·6	1·1
112	8·5	−9·2
132	19·2	−19·4
152	5·0	4·1
172	13·8	13·2
192	3·3	−4·5
1,11,2	14·5	−11·3
1,13,2	<2·4	2·4
1,15,2	<2·1	0·8
212	13·0	−17·4
232	9·7	9·6
252	11·4	11·5
272	12·0	−11·1
292	8·8	−7·2
2,11,2	6·9	−5·7
2,13,2	<2·3	−1·0
2,15,2	3·7	−3·5
312	15·5	−13·2
332	6·3	−7·6
352	2·9	3·1
372	14·0	13·6
392	3·3	−1·2
3,11,2	<2·4	−2·7
3,13,2	3·6	2·2
3,15,2	2·4	3·1
412	<2·2	0·0
432	12·6	−13·8
452	6·0	6·2
472	3·3	4·4
492	<2·4	−1·9
4,11,2	2·7	3·0
4,13,2	1·9	2·6
512	4·4	4·0
532	<2·4	−0·8
552	<2·4	1·7
572	4·7	−4·7
592	<2·0	−2·5
612	2·7	2·8
632	<2·2	1·6
652	<2·0	0·0
672	<1·9	1·0
123	13·5	−17·2
143	5·9	−6·1
163	12·0	11·4
183	<2·1	−1·0
1,10,3	7·7	−7·1
1,12,3	15·8	−14·6
1,14,3	<2·2	1·7
223	<1·8	2·7
243	2·7	−4·3
263	4·7	3·2
283	4·1	2·7
2,10,3	6·7	−5·5
2,12,3	4·0	−1·6
2,14,3	<2·0	−2·2
323	10·4	11·5
343	<2·1	0·0
363	6·7	−9·6
383	<2·3	2·0
3,10,3	10·5	13·8
3,12,3	<2·1	1·4
423	<2·3	−0·3
443	8·7	−8·8
463	8·4	7·6
483	4·8	−5·0
4,10,3	<2·0	0·6
523	8·3	6·7
543	<2·4	0·3
563	8·3	−4·9
583	<2·1	−1·8
623	<2·1	−0·7
643	<2·0	2·1
663	<2·0	1·0
114	10·8	−13·8
134	3·9	5·9
154	6·4	6·2
174	5·4	−6·5
194	6·6	−7·2
1,11,4	6·2	−5·1
1,13,4	2·6	−0·5
214	11·6	−12·5
234	3·2	−4·2
254	<2·2	0·0
274	11·6	11·7
294	<2·4	−2·3
2,11,4	<2·2	−2·1
314	4·5	3·0
334	3·4	−6·2
354	<2·3	0·7
374	<2·4	2·1
394	<2·4	−0·4
3,11,4	4·3	5·1
414	<2·2	0·7
434	<2·3	0·0
454	<2·4	1·4
474	<2·3	−4·0
514	2·8	2·9
534	5·1	4·6
554	<2·0	−2·6
614	<1·9	0·1
125	4·0	5·5
145	3·2	−3·7
165	5·2	2·6
185	<2·4	−2·5
1,10,5	<2·3	−1·5
225	5·8	6·5
245	<2·3	−1·9
265	3·8	−3·5
285	<2·3	0·5
2,10,5	6·9	8·5
2,12,5	<2·1	0·7
325	<2·3	2·3
345	6·2	−7·0
365	6·7	6·2
385	4·5	−5·3
3,10,5	<2·2	2·4
425	6·6	5·9
445	<2·2	−0·2
465	<2·1	−3·2
485	*	−3·0
116	5·6	−6·4
136	<2·3	0·7
156	<2·3	−1·3
176	4·4	5·5
196	<2·1	−0·5
216	4·5	3·6
236	<2·4	−0·6
256	3·7	−2·5
276	<2·3	0·4
316	<2·3	−0·9
336	<2·3	0·6
356	<2·2	0·8
416	2·5	2·2
436	6·1	6·4
456	3·5	−5·0

Table 8 (*cont.*)

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

Plane	$F_{\text{obs.}}$	$F_{\text{calc.}}$
127	<2·3	1·6
147	<2·3	−1·6
167	<2·1	−1·5
227	<2·2	2·5
247	3·4	−3·4
267	3·7	3·5
327	2·5	2·2
021	24·4	−32·0
041	5·2	−7·6
061	25·0	15·2
081	18·0	14·8
0,10,1	8·2	−6·8
0,12,1	12·4	10·6
0,14,1	4·4	3·5
0,16,1	<2·0	1·0
$12\bar{1}$	20·0	−28·5
$14\bar{1}$	<1·2	−0·1
$16\bar{1}$	11·0	10·2
$18\bar{1}$	16·0	11·4
$1,10,\bar{1}$	9·5	−8·6
$1,12,\bar{1}$	18·0	14·1
$1,14,\bar{1}$	<2·3	2·1
$1,16,\bar{1}$	<2·0	0·4
$22\bar{1}$	2·9	−2·6
$24\bar{1}$	12·8	11·8
$26\bar{1}$	22·6	−25·0
$28\bar{1}$	15·4	11·8
$2,10,\bar{1}$	8·0	6·2
$2,12,\bar{1}$	<2·4	0·7
$2,14,\bar{1}$	<2·2	0·6
$32\bar{1}$	11·4	−12·0
$34\bar{1}$	2·5	4·7
$36\bar{1}$	<1·9	0·0
$38\bar{1}$	<2·1	−0·5
$3,10,\bar{1}$	11·0	−9·6
$3,12,\bar{1}$	7·6	−7·1
$3,14,\bar{1}$	<2·0	−1·2
$42\bar{1}$	13·0	−11·2
$44\bar{1}$	3·9	2·4
$46\bar{1}$	<2·1	2·2
$48\bar{1}$	10·0	11·8
$4,10,\bar{1}$	12·0	−10·2
$4,12,\bar{1}$	<2·1	−1·9
$52\bar{1}$	<2·3	3·3
$54\bar{1}$	2·8	3·3
$56\bar{1}$	7·0	−9·0
$58\bar{1}$	3·8	4·7
$5,10,\bar{1}$	3·5	6·0
$5,12,\bar{1}$	2·6	2·8
$62\bar{1}$	<2·4	1·3
$64\bar{1}$	4·7	−4·2
$66\bar{1}$	<2·2	2·0
$68\bar{1}$	<2·0	−0·1
$72\bar{1}$	<2·0	1·1
$74\bar{1}$	<1·9	0·5
012	58·0	−82·0
032	10·0	−11·0
052	9·8	10·6
072	17·6	20·4
092	7·4	5·7
0,11,2	4·7	−3·9
0,13,2	13·4	10·6
0,15,2	4·8	3·3
$11\bar{2}$	7·4	7·5
$13\bar{2}$	6·8	−11·0
$15\bar{2}$	8·3	7·6
$17\bar{2}$	<1·8	−1·2
$19\bar{2}$	<2·1	−2·0
$1,11,\bar{2}$	<2·3	−0·2
$1,13,\bar{2}$	<2·4	−1·4
$1,15,\bar{2}$	<2·1	1·9
$21\bar{2}$	4·9	−12·6
$23\bar{2}$	3·1	2·0
$25\bar{2}$	4·3	−5·2
$27\bar{2}$	<2·0	0·2
$29\bar{2}$	11·4	10·5
$2,11,\bar{2}$	6·7	5·1
$2,13,\bar{2}$	5·0	3·5
$2,15,\bar{2}$	2·8	2·0
$31\bar{2}$	5·0	4·1
$33\bar{2}$	15·4	−18·4
$35\bar{2}$	5·4	4·3
$37\bar{2}$	3·7	4·7
$39\bar{2}$	<2·3	−1·8
$3,11,\bar{2}$	7·9	−6·8
$3,13,\bar{2}$	<2·2	−0·8
$3,15,\bar{2}$	<2·2	1·5
$41\bar{2}$	8·1	−6·8
$43\bar{2}$	<2·1	1·3
$45\bar{2}$	7·9	7·9
$47\bar{2}$	3·7	−6·9
$49\bar{2}$	<2·4	−2·4
$4,11,\bar{2}$	5·0	−5·2
$4,13,\bar{2}$	<1·9	−1·2
$51\bar{2}$	<2·3	−0·1
$53\bar{2}$	<2·3	−1·4
$55\bar{2}$	<2·4	−0·7
$57\bar{2}$	4·2	5·0
$59\bar{2}$	<2·2	1·4
$5,11,\bar{2}$	<1·9	−0·4
$61\bar{2}$	<2·3	−0·2
$63\bar{2}$	10·4	−11·8
$65\bar{2}$	6·0	6·9
$67\bar{2}$	3·4	4·5
$71\bar{2}$	3·8	3·7
023	9·6	12·8
043	4·3	3·6
063	15·0	−16·1
083	8·9	8·0
0,10,3	13·6	12·0
0,12,3	<2·4	−0·2
0,14,3	<2·2	0·6
$12\bar{3}$	8·8	10·5
$14\bar{3}$	4·8	5·9
$16\bar{3}$	6·2	−6·5
$18\bar{3}$	10·6	−9·6
$1,10,\bar{3}$	<2·3	0·8
$1,12,\bar{3}$	5·3	−4·7
$1,14,\bar{3}$	<2·2	−3·0
$22\bar{3}$	4·2	−7·5
$24\bar{3}$	4·2	2·4
$26\bar{3}$	3·8	1·1
$28\bar{3}$	7·4	5·8
$2,10,\bar{3}$	4·8	−4·9
$2,12,\bar{3}$	15·0	13·2
$2,14,\bar{3}$	2·6	0·1
$32\bar{3}$	5·7	−6·3
$34\bar{3}$	6·4	6·1
$36\bar{3}$	10·2	−9·2
$38\bar{3}$	6·5	7·8
$3,10,\bar{3}$	<2·4	0·9
$3,12,\bar{3}$	<2·3	0·5
$42\bar{3}$	3·5	−6·7
$44\bar{3}$	3·5	3·1
$46\bar{3}$	<2·3	−1·2
$48\bar{3}$	<2·4	−0·4
$4,10,\bar{3}$	4·8	−6·4
$4,12,\bar{3}$	3·1	−2·4
$52\bar{3}$	5·1	−7·7
$54\bar{3}$	3·0	2·7
$56\bar{3}$	<2·4	0·3
$58\bar{3}$	5·6	7·5
$5,10,\bar{3}$	5·1	−6·7
$62\bar{3}$	<2·2	1·7
$64\bar{3}$	<2·2	2·2
$66\bar{3}$	2·9	−3·2
$68\bar{3}$	<2·0	3·0
014	2·5	−4·1
034	2·6	−2·7
054	4·5	−2·4
074	5·9	7·0
094	<2·3	−2·0
0,11,4	5·4	−5·3
0,13,4	<2·2	1·4
$11\bar{4}$	49·0	48·8
$13\bar{4}$	7·7	6·4
$15\bar{4}$	6·8	−9·1
$17\bar{4}$	13·8	−17·2
$19\bar{4}$	<2·4	−0·9
$1,11,\bar{4}$	5·1	5·5
$1,13,\bar{4}$	9·2	−8·5
$21\bar{4}$	5·0	4·7
$23\bar{4}$	2·7	−6·0
$25\bar{4}$	5·8	5·1
$27\bar{4}$	2·0	−0·5
$29\bar{4}$	<2·4	−0·5
$2,11,\bar{4}$	3·3	1·8
$2,13,\bar{4}$	3·3	−1·5
$31\bar{4}$	<2·1	2·8
$33\bar{4}$	<2·1	1·2
$35\bar{4}$	5·0	−5·0
$37\bar{4}$	<2·3	−0·7
$39\bar{4}$	5·3	7·3
$3,11,\bar{4}$	3·9	4·7
$41\bar{4}$	6·0	5·6
$43\bar{4}$	4·4	−6·6
$45\bar{4}$	<2·3	1·0
$47\bar{4}$	<2·4	−0·3
$51\bar{4}$	<2·4	−3·2
$53\bar{4}$	<2·4	0·6
$55\bar{4}$	<2·3	3·5
$57\bar{4}$	<1·8	−3·5
$61\bar{4}$	<2·1	1·0
025	4·5	−6·2
045	4·0	−4·1
065	6·4	8·5
085	<2·3	−1·2
0,10,5	<2·4	−2·4
0,12,5	8·9	−9·9

Table 8 (*cont.*)

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

Plane	$F_{\text{obs.}}$	$F_{\text{calc.}}$
$12\bar{5}$	< 2·2	− 3·5
$14\bar{5}$	< 2·2	0·2
$16\bar{5}$	4·8	5·5
$18\bar{5}$	4·1	− 4·9
$1,10,\bar{5}$	4·4	− 4·2
$1,12,\bar{5}$	< 2·1	− 0·1
$22\bar{5}$	< 2·2	0·2
$24\bar{5}$	< 2·3	2·9
$26\bar{5}$	< 2·3	1·2
$28\bar{5}$	3·8	− 4·5
$2,10,\bar{5}$	< 2·2	− 1·3
$2,12,\bar{5}$	< 1·9	− 2·5
$32\bar{5}$	< 2·3	1·0
$34\bar{5}$	< 2·4	1·2
$36\bar{5}$	< 2·4	− 1·8
$38\bar{5}$	< 2·4	2·3
$42\bar{5}$	< 2·4	− 4·5
$44\bar{5}$	< 2·4	2·4
$46\bar{5}$	< 2·4	− 4·3
016	3·7	− 5·1
036	< 2·4	2·3
056	4·5	3·1
076	< 2·4	− 1·2
096	2·7	− 2·9
0,11,6	2·0	− 2·6
$11\bar{6}$	< 2·3	− 0·6
$13\bar{6}$	< 2·3	− 2·2
$15\bar{6}$	< 2·3	3·3
$17\bar{6}$	< 2·4	− 1·6
$19\bar{6}$	< 2·2	− 0·1
$1,11,\bar{6}$	< 2·1	1·6
$21\bar{6}$	19·2	23·5
$23\bar{6}$	< 2·4	4·9
$25\bar{6}$	3·4	− 4·8
$27\bar{6}$	7·0	− 8·3
$29\bar{6}$	< 2·0	− 0·4
$31\bar{6}$	< 2·4	2·6
$33\bar{6}$	< 2·4	− 1·5
$41\bar{6}$	< 2·3	1·7
$51\bar{6}$	< 2·0	3·0
027	4·4	3·5
047	< 2·3	2·1
067	2·2	2·3
$12\bar{7}$	< 2·3	1·3
$14\bar{7}$	< 2·3	1·0
$16\bar{7}$	4·1	− 4·0
$22\bar{7}$	< 2·3	0·9
$31\bar{8}$	8·2	8·0

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The Crystal Structure of Ammonium Trinitrate, $NH_4NO_3 . 2HNO_3$

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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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