Acta Cryst. (1959). **12**, 130

The Crystal and Molecular Structure of Benzamide

By Bruce R. Penfold and J. C. B. White

Chemistry Department, University of Canterbury, Christchurch, C. 1. *New Zealand*

(*Received* 25 *August* 1958)

The crystal structure of a stable form of benzamide has been determined by means of electron-density projections down the two short crystallographic axes. The crystals are monoclinic, space group $P2_1/c$ with $a = 5{\cdot}59$, $b = 5{\cdot}01$, $c = 21{\cdot}93$ Å, $\beta = 90° 45'$. Measurements of bond lengths and angles, with standard deviations of 0·017 Å and 1·0° respectively, have enabled estimates to be made of bond orders in the amide group in which C–N = 1·31, C–O = 1·24 Å. The molecules are non-planar with an angle of 26° between the amide group and benzene ring. The non-planarity is shown to be due to steric hindrance and is discussed in relation to similar molecules of known configuration. Hydrogen bonds connect pairs of molecules into centrosymmetrical dimers which are themselves linked by further hydrogen bonds into endless chains.

1. Introduction

An analysis of the crystal structure of benzamide, $C_6H_5CONH_2$, was undertaken as part of a programme of investigations of the molecular dimensions of simple organic compounds containing an unsubstituted terminal amide group. A particular point of interest with benzamide is the question of whether or not the molecule is planar. In two recent structure determinations, the similar molecules, benzoic acid (Sim, Robertson & Goodwin, 1955) and nicotinic acid (Wright & King, 1953), have been shown to be approximately planar, while nicotinamide (Wright & King, 1954) is not. The results of the present analysis in an approximate form were described by us at the 1957 Dunedin meeting of the Australian and New Zealand Association for the Advancement of Science (Penfold & White, 1957).

2. Experimental

Commercial benzamide was recrystallized from benzene, suitable crystals for X-ray examination being obtained by slow evaporation of the solvent. Crystals of two different forms were found. Crystals of form II consisted of needles and plates, were invariably deformed and were not examined further. Form I crystallized in large blocks, stable at room temperatures, having no particular direction of elongation. The following account refers to form I.

Crystallographic data

Benzamide, C_7ONH_7; monoclinic,

$$a = 5{\cdot}59 \pm 0{\cdot}01,\quad b = 5{\cdot}01 \pm 0{\cdot}01,\quad c = 21{\cdot}93 \pm 0{\cdot}05\ \text{Å}\,,\quad \beta = 90°\,45' \pm 10'\,,$$

axial lengths being determined by the method of Mathieson (1957). Absent spectra: ($h0l$) for l odd and ($0k0$) for k odd, indicating probable space group $P2_1/c$ which was confirmed by the structure analysis. Four molecules per unit cell. Density (calc.) 1·31 g.cm.$^{-3}$, observed 1·28 g.cm.$^{-3}$. Linear absorption coefficient for Cu $K\alpha$ radiation, $\mu = 9{\cdot}0$ cm.$^{-1}$.

Using Cu $K\alpha$ radiation, complete sets of ($h0l$) and ($0kl$) relative intensities were obtained by use of standard Weissenberg techniques and visual comparison of spots with an intensity scale. The data were recorded from two crystals for each zone, the smaller crystals (cross-sectional dimensions 0·34 × 0·24 mm. and 0·39 × 0·17 mm. respectively) being produced by controlled dissolution of much larger crystals in benzene, and being then dipped in liquid air in an attempt to minimize extinction. Intensity data from the large crystals were used only for the weakest reflections.

3. Structure determination and refinement

An attempt was made to solve the structure by the Fourier-transform method, the assumption being made, as with salicylic acid (Cochran, 1953) and benzoic acid (Sim, Robertson & Goodwin, 1955) that pairs of planar molecules would be hydrogen bonded across centres of symmetry to form dimers. This attempt failed, as did also an attempt to interpret the near-origin peaks of the Patterson projection $P(u, w)$, because, as the later analysis showed, the benzamide molecule is far from planar.

Approximate x and z atomic coordinates were eventually determined by successfully accounting for the largest ($h0l$) structure factors of low order. In particular the very intense ($10\bar{4}$) reflection for which the unitary structure factor $U = 0{\cdot}55$, defined the general lie of the molecule. This trial-and-error solution was aided by an optical Fourier synthesizer which was used to perform permutation syntheses (Woolfson, 1954) with the fourteen largest structure factors. These syntheses could be searched rapidly for recognizable benzamide molecules and it was found

Table 1. *Atomic coordinates and temperature factors*

Atom	x	y	z	X' (Å)	Y (Å)	Z' (Å)	α_c	β_c	$\gamma(h0l)$	ψ_c	$\gamma(0kl)$
C_1	0·292	0·031	0·0608	1·610	0·155	1·333	—	—	0·5	—	0·3
C_2	0·478	0·073	0·1086	2·636	0·366	2·382	—	—	0·3	—	0·3
C_3	0·644	0·272	0·1038	3·564	1·363	2·276	—	—	0·5	—	0·8
C_4	0·822	0·296	0·1482	4·544	1·483	3·250	0·5	0·5	(0·75)	32°	0·8
C_5	0·823	0·129	0·1976	4·533	0·646	4·333	0·3	0·8	(0·7)	32°	0·8
C_6	0·647	−0·071	0·2036	3·551	−0·356	4·465	0·5	0·5	(0·75)	32°	0·8
C_7	0·481	−0·097	0·1589	2·638	−0·486	3·485	—	—	0·5	—	0·3
O	0·195	−0·189	0·0530	1·074	−0·947	1·162	0·3	0·8	(0·7)	32°	(0·4)
N	0·230	0·241	0·0284	1·275	1·207	0·623	—	—	0·5	—	0·5

possible to limit the number of sign combinations to four which could then each be tested by actual structure-factor calculation. The optical machine was similar in principle to that described by Woolfson (1954), a modification of the shutter cocking mechanism of the 35 mm. camera body (used instead of Woolfson's film-strip printer) making it possible to take multiple exposures without advancing the film.

Refinements of positional and temperature factor parameters were effected simultaneously by means of repeated difference syntheses (Cochran, 1951). Parameters for atomic temperature factors over and above a general molecular temperature factor are listed in Table 1, the form of the expressions being $\exp[-\gamma \sin^2\theta]$ for isotropic vibrations and $\exp[-\{\alpha_c+\beta_c \sin^2(\varphi-\psi_c)\}\sin^2\theta]$ (Hughes, 1941) for anisotropic vibrations, the terms in the latter expression having the same significance as in the application of Cochran (1951). Structure factors $F(h0l)$ calculated for the atoms with these listed temperature factors were fitted to the observed values by a scaling function s, the 'overall molecular temperature factor' which approximates to $\exp[-3{\cdot}1 \sin^2\theta/\lambda^2]$ and which is given in Table 2.

Table 2. *Overall molecular temperature factor s for F(h0l)*

ξ	0·2	0·4	0·6	0·8	1·0
s	0·98	0·96	0·94	0·89	0·81
ξ	1·2	1·4	1·6	1·8	—
s	0·70	0·59	0·47	0·36	—

Approximate y coordinates for all atoms were assigned from a knowledge of the x and z coordinates and from assumed bond lengths. Refinement using $(0kl)$ structure factors proceeded as for the (010) projection except that assignment of an anisotropic temperature factor was made only for the oxygen atom (the factor being $\exp[-0{\cdot}8 \sin^2\varphi \sin^2\theta]$), random electron-density errors in the final difference map being such as to obscure other fine detail. The scaling function for structure factors $F(0kl)$ approximated to $\exp[-2{\cdot}5 \sin^2\theta/\lambda^2]$.

In both projections, hydrogen atoms were placed at a distance of 1·0 Å from each of the atoms C_3, C_4, C_5, C_6, C_7 on the continuation of a line joining opposite atoms of the benzene ring, and also at one third of the distance from the amide nitrogen atom to a hydrogen bonded oxygen. These hydrogen atoms were included in the calculations of structure factors and their coordinates are listed in Table 3. Final coordinates

Table 3. *Hydrogen coordinates in* Å

Atom	X'	Y	Z'
H_3	3·58	2·01	1·46
H_4	5·26	2·20	3·13
H_5	5·23	0·77	5·02
H_6	3·57	4·03	5·25
H_7	1·93	3·85	3·57
H_{N1}	0·52	1·00	0·04
H_{N2}	1·21	2·18	0·81

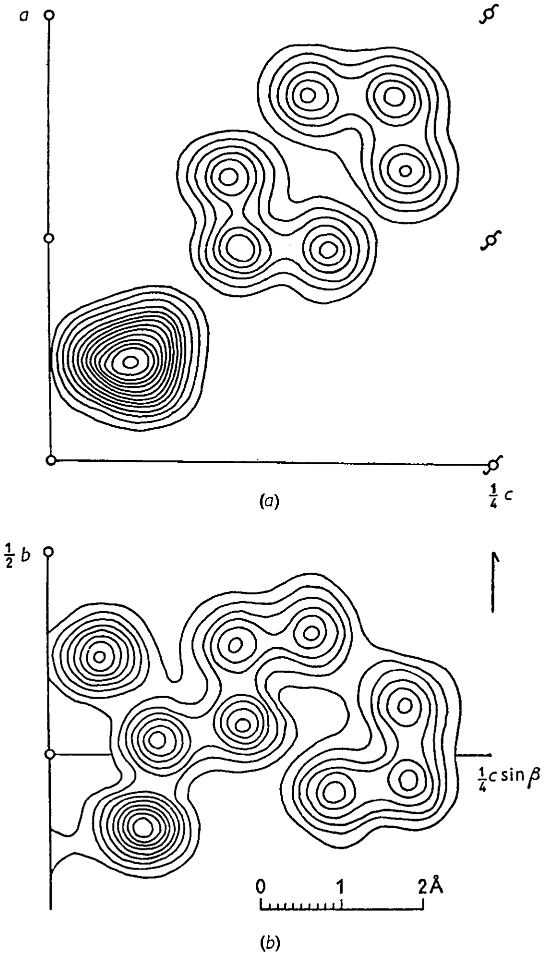

Fig. 1. Electron-density projections (*a*) on (010), (*b*) on (100). Contours at an interval of 1·0 e.Å^{-2}, starting at 2·0 e.Å^{-2}.

Table 4. *Observed and calculated structure factors*

h	k	ℓ	F_o	F_c
0	0	0	—	256
0	0	2	21.1	22.3
0	0	4	23.6	-21.7
0	0	6	6.6	6.0
0	0	8	31.7	-29.2
0	0	10	11.4	-12.0
0	0	12	20.1	-21.1
0	0	14	5.0	-5.1
0	0	16	4.7	-5.9
0	0	18	6.4	6.4
0	0	20	13.7	14.1
0	0	22	9.6	-10.4
0	0	24	5.7	-6.1
0	0	26	<0.6	0.1
0	0	28	0.7	-0.3
1	0	$\bar{28}$	1.4	-1.7
1	0	$\bar{26}$	1.7	-1.9
1	0	$\bar{24}$	2.4	3.1
1	0	$\bar{22}$	3.0	2.9
1	0	$\bar{20}$	0.7	-0.9
1	0	$\bar{18}$	1.6	-1.0
1	0	$\bar{16}$	5.9	-5.0
1	0	$\bar{14}$	5.7	4.3
1	0	$\bar{12}$	16.4	-17.3
1	0	$\bar{10}$	15.7	-13.6
1	0	$\bar{8}$	31.5	26.5
1	0	$\bar{6}$	46.0	49.5
1	0	$\bar{4}$	99.5	119.9
1	0	$\bar{2}$	1.0	0.0
1	0	0	35.0	-36.0
1	0	2	17.6	17.4
1	0	4	50.0	-51.1
1	0	6	27.1	-27.0
1	0	8	47.5	-49.5
1	0	10	14.9	-16.3
1	0	12	9.9	8.1
1	0	14	12.2	12.7
1	0	16	18.4	18.0
1	0	18	16.0	-16.8
1	0	20	6.1	-5.6
1	0	22	8.0	8.6
1	0	24	1.7	-1.8
1	0	26	1.0	0.6
2	0	$\bar{26}$	1.7	2.3
2	0	$\bar{24}$	2.9	3.6
2	0	$\bar{22}$	1.1	-1.6
2	0	$\bar{20}$	0.7	-0.1
2	0	$\bar{18}$	3.7	3.6
2	0	$\bar{16}$	8.3	-9.0
2	0	$\bar{14}$	6.1	-6.6
2	0	$\bar{12}$	22.6	25.4
2	0	$\bar{10}$	20.0	20.6
2	0	$\bar{8}$	15.1	14.1
2	0	$\bar{6}$	17.2	18.4
2	0	$\bar{4}$	5.3	-6.6
2	0	$\bar{2}$	31.0	-31.5
2	0	0	43.8	-44.3
2	0	2	31.3	-32.4
2	0	4	56.7	-55.3
2	0	6	13.4	-12.1
2	0	8	43.2	40.4
2	0	10	6.9	7.8
2	0	12	9.3	8.9
2	0	14	1.0	-0.7
2	0	16	1.1	0.6
2	0	18	8.0	9.1
2	0	20	2.9	-3.1
2	0	22	<0.8	0.1
2	0	24	<0.7	0.4
2	0	26	2.9	1.7
3	0	$\bar{26}$	0.7	-1.1
3	0	$\bar{24}$	<0.6	0.1
3	0	$\bar{22}$	1.0	1.6
3	0	$\bar{20}$	1.9	-2.1
3	0	$\bar{18}$	<0.9	-1.0
3	0	$\bar{16}$	3.7	3.7
3	0	$\bar{14}$	5.1	5.1
3	0	$\bar{12}$	3.0	-0.3
3	0	$\bar{10}$	8.0	9.9
3	0	$\bar{8}$	5.7	-4.7
3	0	$\bar{6}$	35.3	37.1
3	0	$\bar{4}$	14.4	-14.4
3	0	$\bar{2}$	12.9	-15.6
3	0	0	25.1	-26.0
3	0	2	3.7	4.0
3	0	4	30.5	29.0
3	0	6	6.4	6.0
3	0	8	8.9	8.7
3	0	10	20.0	18.4
3	0	12	1.9	1.1
3	0	14	2.9	-2.7
3	0	16	2.9	1.7
3	0	18	<0.9	-0.1
3	0	20	3.1	-3.0
3	0	22	2.6	1.4
3	0	24	2.1	1.6
4	0	$\bar{22}$	0.7	-1.3
4	0	$\bar{20}$	1.9	-3.6
4	0	$\bar{18}$	3.4	4.1
4	0	$\bar{16}$	4.4	3.4
4	0	$\bar{14}$	3.7	-4.7
4	0	$\bar{12}$	6.0	-4.0
4	0	$\bar{10}$	12.8	-13.1
4	0	$\bar{8}$	1.4	0.1
4	0	$\bar{6}$	1.1	0.9
4	0	$\bar{4}$	9.7	-9.7
4	0	$\bar{2}$	5.7	7.3
4	0	0	8.0	8.1
4	0	2	16.9	16.2
4	0	4	11.6	11.6
4	0	6	5.1	5.9
4	0	8	<0.9	1.3
4	0	10	5.9	-5.7
4	0	12	5.6	5.1
4	0	14	2.9	-2.9
4	0	16	10.0	-8.6
4	0	18	1.0	0.9
4	0	20	0.7	-0.4
4	0	22	3.3	-2.3
5	0	$\bar{20}$	1.4	1.7
5	0	$\bar{18}$	4.3	-6.3
5	0	$\bar{16}$	2.3	-0.6
5	0	$\bar{14}$	<0.8	0.7
5	0	$\bar{12}$	<0.9	1.3
5	0	$\bar{10}$	1.1	2.4
5	0	$\bar{8}$	2.9	-3.0
5	0	$\bar{6}$	3.4	4.1
5	0	$\bar{4}$	3.7	3.1
5	0	$\bar{2}$	14.7	14.7
5	0	0	3.7	4.1
5	0	2	13.0	-11.7
5	0	4	7.3	7.9
5	0	6	1.4	0.3
5	0	8	1.4	-2.3
5	0	10	4.7	-4.4
5	0	12	9.7	-9.3
5	0	14	<0.8	0.4
5	0	16	2.1	-1.0
5	0	18	<0.6	0.4
5	0	20	1.9	0.1
6	0	$\bar{14}$	<0.5	0.6
6	0	$\bar{12}$	<0.6	-0.6
6	0	$\bar{10}$	2.4	2.6
6	0	$\bar{8}$	2.9	2.3
6	0	$\bar{6}$	3.7	3.1
6	0	$\bar{4}$	3.1	-2.1
6	0	$\bar{2}$	9.0	-8.8
6	0	0	9.1	8.9
6	0	2	2.6	1.9
6	0	4	7.4	-7.9
6	0	6	3.0	-2.3
6	0	8	5.1	-5.1
6	0	10	1.0	0.6
6	0	12	1.6	0.0
6	0	14	0.7	0.6
7	0	$\bar{6}$	1.3	-1.1
7	0	$\bar{4}$	2.3	2.4
7	0	$\bar{2}$	<0.5	0.6
7	0	0	3.1	-3.9
7	0	2	0.7	-0.6
7	0	4	1.7	-1.4
7	0	6	1.0	0.7
0	1	1	37.6	50.8
0	1	2	30.1	-33.5
0	1	3	26.0	-26.7
0	1	4	2.7	-3.4
0	1	5	15.0	13.3
0	1	6	16.2	16.7
0	1	7	30.1	-29.1
0	1	8	6.1	4.9
0	1	9	5.6	-6.3
0	1	10	20.6	-22.5
0	1	11	1.2	-0.2
0	1	12	23.0	-23.5
0	1	13	8.7	-8.5
0	1	14	9.7	-10.2
0	1	15	6.8	6.3
0	1	16	4.6	-6.3
0	1	17	3.6	3.2
0	1	18	2.9	2.4
0	1	19	10.4	11.4
0	1	20	2.4	2.9
0	1	21	2.4	-1.7
0	1	22	2.4	-1.7
0	1	23	5.3	-7.5
0	1	24	3.6	4.4
0	1	25	1.5	1.2
0	1	26	4.1	6.1
0	1	27	1.5	-2.2
0	2	0	23.8	-25.5
0	2	1	12.1	12.4
0	2	2	22.3	-22.5
0	2	3	8.7	10.2
0	2	4	7.3	-5.1
0	2	5	5.1	-4.1
0	2	6	8.7	-7.0
0	2	7	15.3	15.8
0	2	8	9.5	-9.2
0	2	9	12.4	10.7
0	2	10	10.2	10.9
0	2	11	15.5	-16.5
0	2	12	2.7	5.1
0	2	13	5.6	-4.6
0	2	14	9.5	7.3
0	2	15	5.1	4.9
0	2	16	9.0	9.0
0	2	17	4.1	-6.1
0	2	18	4.1	5.6
0	2	19	2.9	-1.9
0	2	20	1.7	0.5
0	2	21	1.7	1.5
0	2	22	3.4	-2.9
0	2	23	<1.3	-0.7
0	2	24	1.9	1.0
0	2	25	1.9	1.9
0	3	1	3.4	-2.9
0	3	2	5.1	4.6
0	3	3	8.0	-8.0
0	3	4	13.6	-12.4
0	3	5	10.7	-10.9
0	3	6	<1.3	-1.2
0	3	7	5.1	6.5
0	3	8	12.6	12.8
0	3	9	5.3	6.5
0	3	10	5.6	5.6
0	3	11	1.7	2.4
0	3	12	5.8	3.4
0	3	13	5.1	5.3
0	3	14	11.4	12.4
0	3	15	1.9	0.2
0	3	16	4.6	5.6
0	3	17	<1.5	0.2
0	3	18	4.4	-5.1
0	3	19	<1.4	0.2
0	3	20	2.2	-1.7
0	3	21	1.7	-0.5
0	3	22	2.2	-2.4
0	3	23	1.5	-1.9
0	3	24	1.9	-2.7
0	4	0	7.0	4.4
0	4	1	4.4	-4.6
0	4	2	13.3	13.3
0	4	3	17.0	-19.4
0	4	4	2.4	2.7
0	4	5	8.2	-7.5
0	4	6	4.1	-5.1
0	4	7	4.4	4.1
0	4	8	1.9	2.7
0	4	9	1.9	-2.4
0	4	10	2.9	-3.9
0	4	11	2.4	3.2
0	4	12	<1.5	-1.9
0	4	13	4.4	3.9
0	4	14	2.4	-1.9
0	4	15	6.3	7.0
0	4	16	<1.4	-0.5
0	4	17	3.4	3.4
0	4	18	<1.2	-0.2
0	4	19	1.5	-1.7
0	4	20	1.9	-1.9
0	4	21	2.7	-2.7
0	4	22	1.9	0.7
0	5	1	1.9	0.5
0	5	2	6.3	-5.8
0	5	3	12.1	13.3
0	5	4	11.2	-11.6
0	5	5	<1.5	-0.5
0	5	6	<1.5	0.5
0	5	7	6.3	-5.8
0	5	8	2.7	-2.2
0	5	9	6.1	-5.3
0	5	10	2.9	-2.2
0	5	11	4.4	-4.4
0	5	12	<1.3	-0.5
0	5	13	<1.2	-1.2
0	5	14	<1.1	-0.7
0	5	15	2.9	2.2
0	5	16	3.6	3.6
0	5	17	2.9	3.4
0	6	0	4.6	-3.4
0	6	1	<1.1	1.9
0	6	2	<1.1	1.2
0	6	3	<1.0	-0.5
0	6	4	1.5	1.9
0	6	5	<1.0	-0.2
0	6	6	1.9	-1.7
0	6	7	<0.9	0.5
0	6	8	2.9	-2.7
0	6	9	1.2	-0.7
0	6	10	2.7	-2.9

x, y, z for C, N and O atoms are listed as fractions of the-unit cell edges in Table 1. In the same table, X', Y, Z' are coordinates in Ångström units referred to orthogonal axes a, b and c', such that $X' = X + Z \cos \beta$ and $Z' = Z \sin \beta$. Observed and calculated structure factors are listed in Table 4. Values for $R = \Sigma \| F_{\text{obs.}} | - | F_{\text{calc.}} \| \div \Sigma | F_{\text{obs.}} |$ were $R(h0l) = 0{\cdot}087$ for all observed reflections except $(10\bar{4})$, and $R(0kl) = 0{\cdot}115$ for all observed reflections except (011). These two reflections were the most intense in their respective zones and had values of $F|_{\text{obs.}}| - |F_{\text{calc.}}|$ 23 times and 16 times the respective averages, the observed value being low in each case. It was concluded that their intensities had been reduced by extinction. In deriving the final electron-density maps shown in Fig. 1, the calculated values of these two structure factors were used in the Fourier syntheses. Omission of hydrogen atoms from the calculations caused R to rise to 0·106 and 0·146 for the $(h0l)$ and $(0kl)$ zones respectively. In Fig. 2 is shown the final difference map derived by subtracting all atoms but the hydrogens from $\varrho_{\text{obs.}}$. This map serves to confirm the expected positions for all H atoms except H_{N2} which is involved in a hydrogen bond. Electron-density errors are expected to be high in this region where the amide group is unresolved and there is no direct evidence for the exact position of H_{N2}.

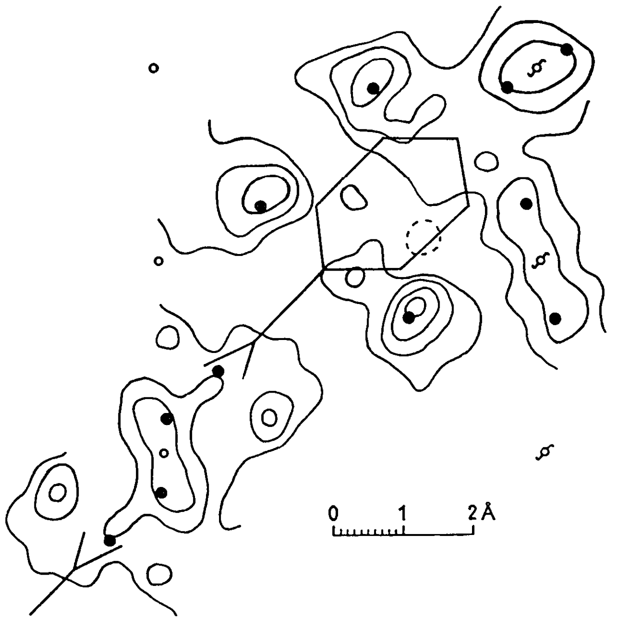

Fig. 2. Projection of electron-density on (010) from which the contributions of C, N and O atoms have been subtracted. Calculated positions of H atoms are indicated by black dots. Contours at 0·2, 0·4, 0·6, 0·8 e.Å^{-2}, negative contour broken.

4. Accuracy

Standard deviations in electron density and in atomic coordinates were estimated by the method of Cruickshank (1949). ΔF, the error in the F values, has been taken to be $|F_{\text{obs.}}|-|F_{\text{calc.}}|$. Standard deviations in electron density $\sigma(\varrho_0)$ are 0·20 e.Å^{-2} for the (010) projection and 0·25 e.Å^{-2} for the (100) projection. Standard deviations in coordinates are

$\sigma(x)=\sigma(z)=0{\cdot}010$ Å, $\sigma(y)=0{\cdot}015$ Å for carbon,
$\sigma(x)=\sigma(z)=0{\cdot}009$ Å, $\sigma(y)=0{\cdot}013$ Å for nitrogen,
$\sigma(x)=\sigma(z)=0{\cdot}008$ Å, $\sigma(y)=0{\cdot}012$ Å for oxygen.

Hence standard deviations in all bond lengths will be approximately 0·017 Å, taking into account the fact that the C–O and C–N bonds are nearly parallel to the b axis. The standard deviation in bond angle is 1·0° as determined by the method of Ahmed & Cruickshank (1953).

5. Description of structure

Bond lengths and angles of the benzamide molecule are shown in Fig. 3. The benzene ring is well described by the equation $4{\cdot}433X'-4{\cdot}735Y-3{\cdot}708Z'-1=0$ which represents a plane. The r.m.s. distance of the ring atoms from this plane is 0·014 Å. Distances of all atoms from the plane are listed in Table 5, only C_1, N and O showing significant departures. In the group C_2C_1NO, none of the atoms deviates by as much as 0·01 Å from the mean plane $3{\cdot}203X'-1{\cdot}040Y-2{\cdot}967Z'-1=0$. The molecule can therefore be described as a plane benzene ring and a plane amide group twisted about the connecting bond C_1–C_2, the angle of intersection of the two planes being 26°.

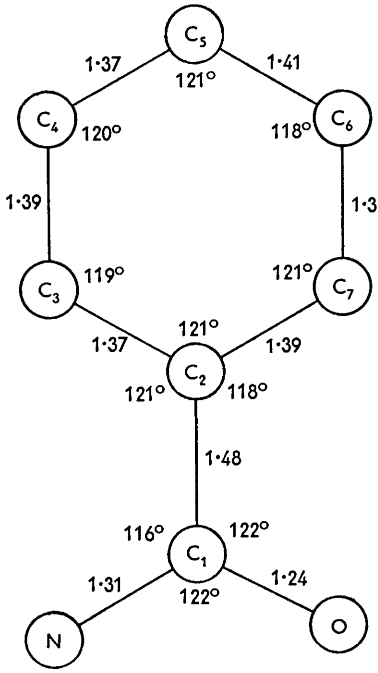

Fig. 3. Bond lengths and bond angles in the benzamide molecule, represented as a plane for convenience.

Table 5. *Distances of atoms from mean plane of benzene ring*

Atom	Δ	Atom	Δ
C_1	+0·06 Å	C_6	−0·017 Å
C_2	+0·016	C_7	+0·007
C_3	−0·012	O	+0·53
C_4	+0·010	N	−0·45
C_5	−0·004		

The two views along the b and a axes of the arrangement of benzamide molecules in the crystal are shown in Fig. 4. The molecules are connected by two sets of N–H · · · O type hydrogen bonds, the first set of length 2·96 Å joining pairs of molecules across centres of symmetry to form dimers, and the second set of length 2·91 Å joining such dimers into endless chains extended along the b axis. On account of their non-planarity the molecules exist in right- and left-handed forms, there being two of each form in the unit cell. The two hydrogen-bond angles C_1–N–O′ are 117° for the bonds across the centre of symmetry involving H_{N1}, and 134° for bonds involving H_{N2}. Of the other intermolecular-approach distances (not involving hydrogen), the shortest is that of 3·51 Å joining N of one molecule to C_4 of another separated from the first by a translation a.

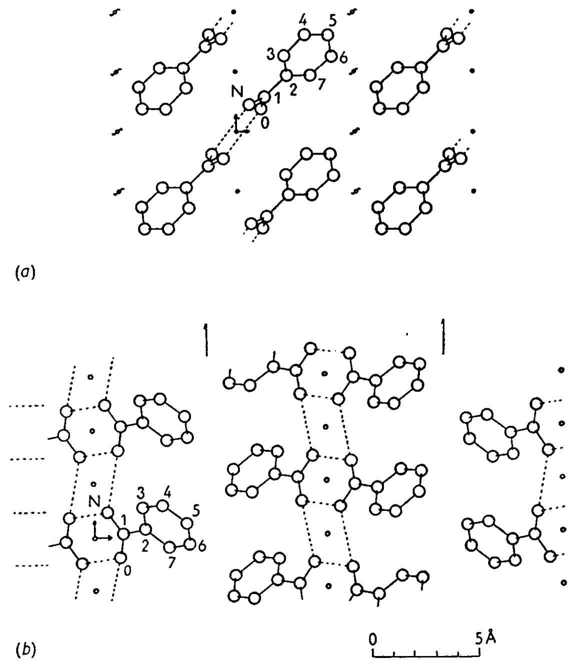

Fig. 4. Views of the arrangement of molecules (*a*) along the *b* axis, (*b*) along the *a* axis showing hydrogen bonds as broken lines.

6. Discussion

Molecular dimensions

None of the bonds of the benzene ring differ significantly from each other or from the mean observed value of 1·38 Å, a value which itself does not differ significantly from the accepted value of 1·39 Å. The ring does not depart significantly from planarity, but the results of the extended refinement of the anthracene structure (Robertson, 1958), where one carbon atom is significantly displaced from the mean molecular plane, suggest that planarity is not necessarily to be expected of aromatic rings whose atoms have close intermolecular contacts in the crystal setting. The bond length C_1–C_2, at 1·48 Å is significantly less than 1·54 Å the standard length for single bonds. It is the same length as the corresponding bond in the analogous compounds benzoic acid (Sim, Robertson & Goodwin, 1955) and nicotinic acid (Wright & King, 1953) although in nicotinamide (Wright & King, 1954) the observed length is 1·52 Å. Shortening in this bond has been interpreted to mean that there is some double-bonded character consequent upon resonance between the amide (or carboxyl) group and the ring. The observed length of 1·53 Å for the C–CH_3 bonds in hexamethyl benzene (Brockway & Robertson, 1939) suggests that there is very little shortening of bonds attached to aromatic rings when there is no possibility of resonance. Confirmation of this from structures refined by modern Fourier techniques would be desirable. We shall, however, in the following discussion assume that the shortening in the bond C_1–C_2 is due to some double-bond character.

The bond lengths and angles in the amide group may be discussed profitably with the aid of the extensive compilation of data for amides made by Hahn (1957) who has examined the relationship of both bond lengths and of bond angles to bond order. He has assumed standard bond lengths C=O, 1·205; $C-O^{(-)}$, 1·425; $C=N^{(+)}$, 1·235; C–N, 1·475. In Table 6 are listed the amide bond lengths and angles for benzamide together with the values calculated as described by Hahn (1957). This table may be compared with Hahn's Table 7. The order of agreement is satisfactory.

Table 6. *Observed and calculated bond lengths and angles in the benzamide amide group*

Bond or angle	Observed	Double bond character (%) with calculated lengths and angles	
C_1–C_2	1·48 Å	10%	1·49 Å
C_1–N	1·31	35	1·32
C_1–O	1·24	55	1·25
O–C_1–N	122°	90	123·6°
C_2–C_1–N	116	26	115·2
C_2–C_1–O	122	64	121·2

Molecular configuration

It is on the overall molecular configuration of benzamide that this structure analysis provides the most significant and perhaps the most useful information. Of those compounds whose crystal structures are known, nicotinamide, nicotinic acid and benzoic acid are the most closely related chemically. The benzamide configuration will be compared with these three. In the two acids, the oxygen atoms show small but significant displacements from the plane of the ring, the average displacements being 0·035 Å for benzoic acid and 0·075 Å for nicotinic acid i.e. there is a very small angle of twist (< 4°) between carboxyl group and ring. The two amides show large displacements for the nitrogen and oxygen atoms, the averages being 0·45 Å for nicotinamide and 0·49 Å for benzamide, corresponding to twists of the amide groups away from planarity of 24° and 26° respectively. An examination for these compounds of the non-bonded approach distances of the amide and carboxyl groups to the ortho carbon and hydrogen, C_3 and H_3, proves enlightening. In Table 7 are listed the observed distances H_{N2}–H_3, H_{N2}–C_3 and N–C_3 for benzamide and nicotinamide, together with the corresponding O–C_3 distances in benzoic acid and nicotinic acid. The coordinates used for H_{N2} have in both cases been calculated assuming that these atoms are 1·0 Å from the amide nitrogen on the straight line joining it to its hydrogen bonded oxygen. Also listed in the table are the distances between the same pairs of atoms calculated for molecules which have no twist about C_1–C_2 (numbering as in this paper) and in which the angle H_{N2}–N–C_1 is assumed the same as before (123° for nicotinamide and 134° for benzamide). This last assumption has been made so that differences between the two sets of distances listed are likely to be as nearly as possible the result of the twist about C_1–C_2 and not of any distortion of the –NH_2 group by hydrogen bonds. The indications are that the two amides are sterically hindered, a planar configuration being unstable because of the consequent close approaches (1·97 Å and 1·94 Å) of non-bonded

Table 7. *Observed and calculated non-bonded approaches in Å*

		Calculated for planar molecule	
	Observed	For observed C–N–H angle	For C–N–H = 120°
Benzamide:			
H_{N2}–H_3	2·46 Å	1·97 Å	1·74 Å
H_{N2}–C_3	2·89	2·63	2·38
N–C_3	2·83	2·78	—
Benzoic acid:			
O–C_3	2·79	—	—
Nicotinamide:			
H_{N2}–H_3	2·19	1·94	1·90
H_{N2}–C_3	2·70	2·55	2·50
N–C_3	2·92	2·88	—
Nicotinic acid:			
O–C_3	2·81	—	—

hydrogen atoms. No such hindrance need occur in the two acids. We conclude that the steric effect opposing planarity in the amides must be greater in magnitude than the resonance effect stabilising the planar structure (Wheland, 1955). Resonance in sterically hindered aromatic molecules has been examined by Adrian (1958) and a semi-empirical method for treating such molecules developed, so that predictions can be made for the angle of twist on the basis of assumed steric interaction energies and resonance energies. Using Adrian's curves relating the interaction energies of non-bonded pairs of atoms, E_{H-H} and E_{C-H}, with their separations, we derive the following facts. As a result of the twist in molecules of benzamide and nicotinamide, there are losses of steric interaction energy as follows.

For benzamide $E_{H_{N2}-H_3}$ falls by 0·6 kcals/mole and $E_{C_3-H_3}$ falls by 0·3 kcals/mole.

For nicotinamide $E_{H_{N2}-H_3}$ falls by 0·4 kcals/mole and $E_{C_3-H_3}$ falls by 0·4 kcals/mole.

Relative to a planar and symmetrical $-NH_2$ group with all angles 120°, the corresponding energy losses are for benzamide 1·6 and 0·8 kcals/mole and for nicotinamide 0·5 and 0·4 kcals/mole.

The situation is complicated by the formation of two hydrogen bonds per molecule, each of energy approximately 2 kcals/mole (Davies, 1946), so the non-bonded interaction energy may have been reduced not only by twisting about C_1–C_2 but also by distortion of the $-NH_2$ group as a result of hydrogen bond formation. It is therefore not possible to make quantitative predictions about the angle of twist. However it seems highly probable that a twist of some magnitude in these amides is required by steric hindrance.

We are indebted to Mr R. H. Nokes, senior technician of this department, who designed and built the optical Fourier synthesizer. Some of the computations were carried out on SILLIAC, the University of Sydney computer, and in this connection we are very grateful for the cooperation received from the director and staff of the Adolph Basser Computing Laboratory, and also from Dr H. C. Freeman and Mr J. E. W. L. Smith of the Department of Chemistry who were good enough to check our work. Programmes used were those described by Freeman (1958). We also acknowledge a grant from the Research Fund Committee of the University of New Zealand.

References

ADRIAN, F. J. (1958). *J. Chem. Phys.* **28**, 608.
AHMED, F. R. & CRUICKSHANK, D. W. J. (1953). *Acta Cryst.* **6**, 385.
BROCKWAY, L. O. & ROBERTSON, J. M. (1939). *J. Chem. Soc.* **142**, 1324.
COCHRAN, W. (1951). *Acta Cryst.* **4**, 81.
COCHRAN, W. (1953). *Acta Cryst.* **6**, 260.
CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.
DAVIES, M. M. (1946). *Ann. Rep. Progr. Chem.* **43**, 6.
FREEMAN, H. C. (1958). *Aust. J. Chem.* **11**, 99.
HAHN, T. (1957). *Z. Kristallogr.* **109**, 438.
HUGHES, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.
MATHIESON, A. McL. (1957). *Acta Cryst.* **10**, 351.
PENFOLD, B. R. & WHITE, J. C. B. (1957). *Aust. J. Sci.* **19**, 33.
ROBERTSON, J. M. (1958). *Rev. Mod. Phys.* **30**, 155.
SIM, G. A., ROBERTSON, J. M. & GOODWIN, T. H. (1955). *Acta Cryst.* **8**, 157.
WHELAND, G. W. (1955). *Resonance in Organic Chemistry.* New York: Wiley.
WOOLFSON, M. M. (1954). *Acta Cryst.* **7**, 65.
WRIGHT, W. B. & KING, G. S. D. (1953). *Acta Cryst.* **6**, 305.
WRIGHT, W. B. & KING, G. S. D. (1954). *Acta Cryst.* **7**, 283.