Evidently packing in the structure is good and all contacts are substantially normal.

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The Crystal Structure of 4-*iso*Propylidene–Aminophenol

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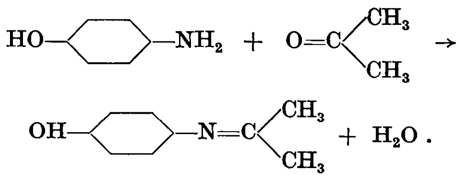
The crystals obtained from a solution of *p*-aminophenol in acetone are shown to be a condensation compound, 4-*iso*propylidene–aminophenol (space group $P22_12_1$, $a = 5{\cdot}74$, $b = 12{\cdot}01$, $c = 12{\cdot}16$ Å). A detailed crystal-structure analysis by means of Fourier syntheses of the electron density projected perpendicular to the *a*, *b* and *c* axes is given. Bond lengths and bond angles in the molecule have been calculated and lie close to the accepted values (the standard deviation of a bond length is 0·04 Å). The molecules of 4-*iso*propylidene–aminophenol are linked into infinite chains running parallel to the *b* axis by hydrogen bonds of length 2·66 Å between the nitrogen and oxygen atoms of adjacent molecules.

Introduction

Caspari (1927) stated that *p*-aminophenol existed in two forms, an α-form crystallized from ethyl alcohol and a β-form from acetone. Analysis of samples of the two forms prepared in the way described showed that only the α-form had the appropriate empirical formula C_6H_7ON; the empirical formula of the β-form was almost exactly $C_9H_{11}ON$, indicating that the acetone had reacted with the *p*-aminophenol. The reaction is described in *Beilsteins Handbuch* (1929); condensation occurs and results in the formation of 4-*iso*propylidene–aminophenol:



The structure analysis of the condensation product is described in the present paper; a three-dimensional structure analysis of the parent substance has been given by Brown (1951).

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Preliminary investigations

Crystals of 4-*iso*propylidene–aminophenol were prepared by dissolving BDH *p*-aminophenol in acetone. Practically colourless needle-like crystals of hexagonal cross-section can be obtained by warming the blood-red solution over bone charcoal. The needle axis is the *a* axis, and the faces developed are (011) and $(01\bar{1})$ (prominent) and less frequently (010). The goniometrically observed axial ratio was 1·02, in good agreement with the value 1·012 calculated from the X-ray cell dimensions. The crystals are optically positive and the vibration direction of greatest refractive index lies along the *b* axis; they have a good cleavage parallel to (100). The cell dimensions and space-group, determined from heavily exposed Weissenberg photographs calibrated with lines from a copper wire specimen, were

$$a = 5{\cdot}74\pm0{\cdot}02,\quad b = 12{\cdot}01\pm0{\cdot}04,\quad c = 12{\cdot}16\pm0{\cdot}04\ \text{Å}\,.$$

Absences: $0k0$ for $k \neq 2n$, $00l$ for $l \neq 2n$. The space group is $P22_12_1$. The observed density was 1·162 g.cm.$^{-3}$ so there are 4 molecules per unit cell of $C_9H_{11}ON$ (calculated 3·94). The linear absorption coefficient is 7·2 cm.$^{-1}$.

These results may be compared with those of Caspari: cell dimensions 5·82, 11·85 and 12·07 Å; 6 molecules (supposedly of *p*-aminophenol) per unit cell; no absences; suggested space groups *Pmm* or *Pmmm*.

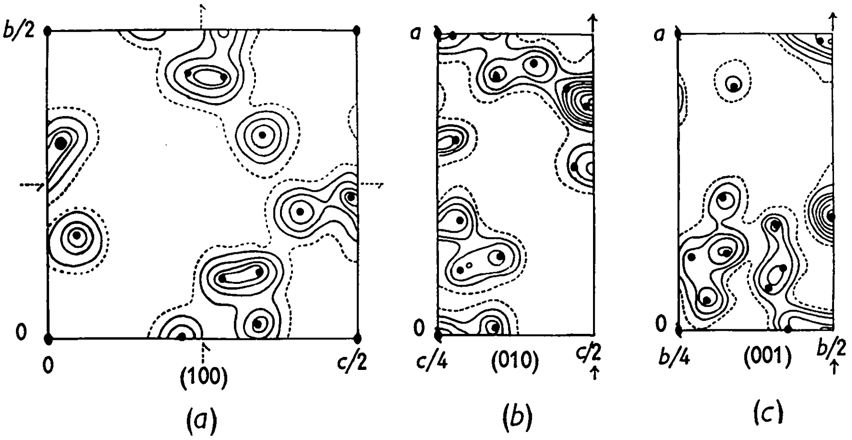
Experimental

The crystals deteriorate slowly in air and become white and opaque owing to hydrolysis back to *p*-aminophenol and acetone, but good X-ray photographs can be obtained before the break-up of the crystal lattice becomes serious. For the *a*-axis photographs a needle 1 mm. long and with a square cross-section of side 0·25 mm. was used. For the *b*- and *c*-axis photographs a 0·5 mm. length was cut from a needle crystal of square cross-section and of side 0·5 mm. This rough cube was mounted about each of its (100) face diagonals in turn. From these specimens, sets of relative zero-layer intensities were obtained with Weissenberg cameras and the use of the multiple-film technique (Robertson, 1943). No correction was made for absorption in the specimens as they were small and roughly equidimensional. The intensities were put on an absolute scale by Wilson's method (Wilson, 1942). The strongest reflexion, (022), had an $\hat{F}$ value (Harker & Kasper, 1948) of 0·3.

Determination of the structure

The $0kl$ projection was examined first; structure-factor graphs (Bragg & Lipson, 1936) were drawn for ten reflexions which had outstandingly large or small $\hat{F}$'s and the approximate position of the molecule in the cell was established. Small shifts were then made to improve the agreement between observed and calculated structure factors, and rough electron density maps were prepared by Fourier syntheses containing only the low-order observed structure factors. The first model to give a recognizable benzene ring in the electron-density map had a reliability (R) factor of 77%. The R-factor dropped to 31% as a result of refinement by F_o syntheses. Further refinement of the atomic co-ordinates deduced from this projection was carried out with the use of F_o-F_c syntheses (Cochran, 1951). The final projected electron-density map is shown in Fig. 1(*a*) and the final difference synthesis in Fig. 2(*a*).

From the approximate form of the molecule, the known *y*, *z* co-ordinates, and a consideration of the observed ($h00$) structure factors, the displacement of the molecule along the *a* axis was deduced and a set of *x* co-ordinates was derived. The *x* and *z* co-ordinates were refined by calculation of projected electron-density maps and by F_o-F_c syntheses. The final electron-density map and difference synthesis are shown in Figs. 1(*b*) and 2(*b*) respectively.



(*a*) (*b*) (*c*)

Fig. 1. Final projected electron density maps for $C_9H_{11}ON$. Contours at arbitrary equal intervals; zero contour broken. Final atomic positions: ●.

As an additional check on the correctness of the structure, the structure factors for the third projection were evaluated on the basis of the x and y co-ordinates deduced from the other two projections. One map of the electron density projected perpendicular to the c axis was calculated (Fig. 1(c)).

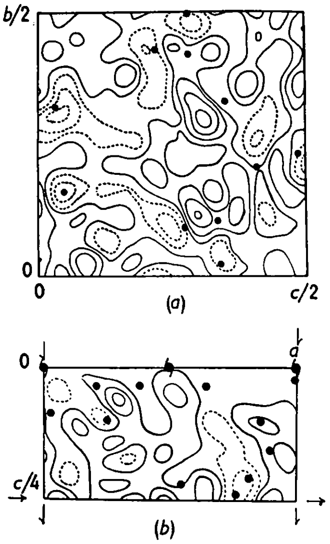


Fig. 2. Final difference syntheses for $C_9H_{11}ON$. Negative contours broken. Final atomic positions: ●. (a) Contours at intervals of $\frac{1}{4}$ e.Å^{-2}. (b) Contours at intervals of $\frac{1}{2}$ e.Å^{-2}.

Results of the structure analysis

Table 1 gives the atomic co-ordinates, Table 2 the reliability factors of the three projections and Table 3 some standard deviations. Lists of calculated and observed structure factors are given in a thesis (Holmes, 1952).

Table 1. *Atomic co-ordinates*

Atom	x	y	z
C_1	0·785	0·923	0·214
C_2	0·993	0·929	0·272
C_3	0·024	0·019	0·343
C_4	0·856	0·104	0·343
C_5	0·646	0·098	0·284
C_6	0·617	0·006	0·214
C_7	0·760	0·231	0·487
C_8	0·819	0·340	0·543
C_9	0·557	0·171	0·530
N	0·902	0·202	0·405
O	0·738	0·830	0·151

Table 2. *Reliability factors*

Projection	R (%)
$0kl$	19·9
$h0l$	22·0
$hk0$	27·7

Table 3. *Standard deviations*

From $0kl$ $\sigma(y) = 0{\cdot}018$ Å.
$\sigma(z) = 0{\cdot}018$ Å.
$\sigma(\varrho) = 0{\cdot}23$ e.Å^{-2}.
From $h0l$ $\sigma(x) = 0{\cdot}042$ Å.
$\sigma(z) = 0{\cdot}040$ Å.
$\sigma(\varrho) = 0{\cdot}46$ e.Å^{-2}.

The bond lengths and bond angles calculated from these atomic co-ordinates are given in Table 4 and some intermolecular distances are listed in Table 5. Since the y and z co-ordinates were deduced from the $0kl$ projection and the x co-ordinates from the $h0l$ projection, the standard deviation of an atomic position is 0·049 Å and that of a bond length is 0·04 Å. When the plane of the benzene ring is taken as the ground plane the azimuthal angle of the line N–C_7 with respect to the line C_4–N is 30° and the angle of elevation is 49°.

Table 5. *The shorter intermolecular distances*

N–O′ = 2·66 Å
C_8–O′ = 3·47
C_7–O′ = 3·54
C_9–C_2' = 3·67
C_8–C_6' = 3·74 Å
C_8–C_3' = 4·03
C_8–C_8' = 3·98

(Atoms marked with a dash lie in an adjacent molecule.)

The angle between the lines N′–O and C_1–O is 118° and that between the lines N′–O and C_4'–N′ is 119°. The equation of the plane containing the benzene ring,

$$x+1{\cdot}0494y-1{\cdot}6507z-11{\cdot}8889 = 0\,,$$

was obtained by the method of least squares. When the co-ordinates of the nitrogen and oxygen atoms were included in the least-squares analysis the equation derived was:

$$x+0{\cdot}9976y-1{\cdot}7004z-11{\cdot}1003 = 0\,.$$

The distance from this plane of the atoms of the benzene ring and of the nitrogen and oxygen atoms

Table 4. *Bond lengths and angles*

C_1–C_2 = 1·39 Å
C_2–C_3 = 1·40
C_3–C_4 = 1·40
C_4–C_5 = 1·40
C_5–C_6 = 1·40
C_6–C_1 = 1·39
Sides of benzene ring; mean = $1{\cdot}39_7$ Å.
C_1–O = 1·38
C_4–N = 1·42
N–C_7 = 1·33
C_7–C_8 = 1·51
C_7–C_9 = 1·47

C_1–C_2–C_3 = 118°
C_2–C_3–C_4 = 118
C_3–C_4–C_5 = 124
C_4–C_5–C_6 = 117
C_5–C_6–C_1 = 119
C_6–C_1–C_2 = 124
Angles of benzene ring
C_4–N–C_7 = 120
C_8–C_7–C_9 = 119½
C_8–C_7–N = 115
C_9–C_7–N = 129

are less than 0·05 Å, indicating that these atoms are coplanar within the limits of experimental error.

Description of the structure

4-*iso*Propylidene–aminophenol has a simple hydrogen-bonded molecular structure; the three principal projected views of the contents of one unit cell are shown in Fig. 3. The hydrogen bonds of length 2·66 Å join the nitrogen atom of one molecule to the oxygen atom of a molecule related to the first by a twofold screw axis parallel to *b*. Two of these chains of bonded molecules thread the cell in opposite directions. All the possibilities for hydrogen bonding have been utilized in forming the chains of molecules so there can be no links between the chains. The physical properties of the substance, namely, good cleavage perpendicular to the *a* axis and positive birefringence with the vibration direction of greatest refractive index along *b*, are in accordance with the proposed structure. In agreement also is the observation that planes approximately perpendicular to the *b* axis have a lower temperature factor than all other planes, indicating that the thermal molecular vibrations are of smallest amplitude in this direction.

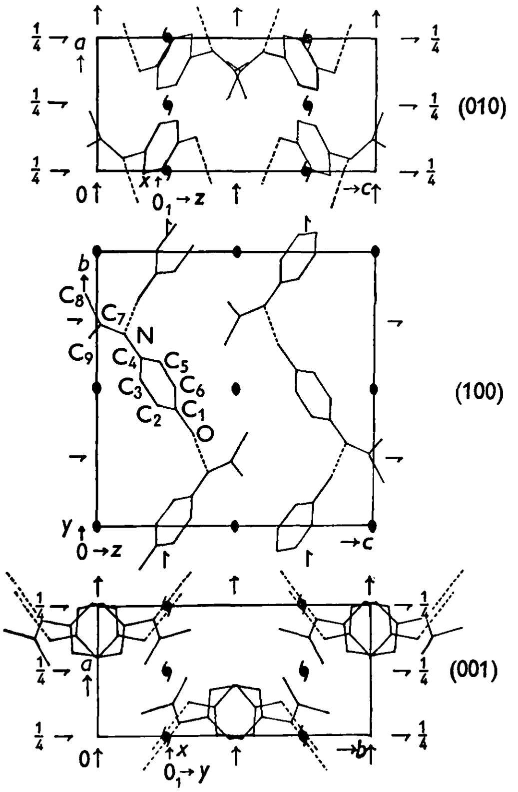


Fig. 3. Appearance of the three principal projections of $C_9H_{11}ON$. Hydrogen bonds shown by broken lines.

Discussion

The accuracy obtained in the present structure analysis is rather low owing to the bad overlapping which occurs in all three projections, but the position has been somewhat improved by the intensive use of $F_o - F_c$ syntheses. The bond lengths and bond angles, except in the *iso*propylidene amino group, are close to the expected values. The deviations in this part of the molecule can hardly be considered significant although Fig. 4 shows that they resemble those observed in acetoxime (Bierlein & Lingafelter, 1951). The C–N=C angle is 120°, very close to the values found in melamine (Hughes, 1941) and in pyrimidines (Pitt, 1945). The hydrogen bond length of 2·66 Å is shorter than any N · · · HO distance given in the recent review by Brown (1951) but is greater than the values lately determined in guanine hydrochloride (2·62 Å) (Broomhead, 1951) and in cysteylglycine sodium iodide (2·55 Å) (Dyer, 1951). Table 5 shows that there are no other close intermolecular contacts.

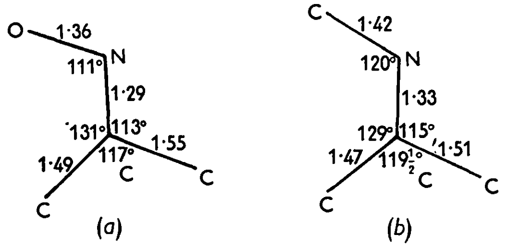


Fig. 4. (*a*) Acetoxime. (*b*) *iso*Propylidene amino-group.

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