contacts between the molecular sheets, and is in turn related to the large thermal coefficient of *c*. Bond distances have been corrected for effects of rigid-body libration and for the neutron results corrected values are about 0·002 Å longer than uncorrected values for the pyrimidine ring and 0·001 Å for the furanose ring.

The thermal motions of individual atoms are illustrated in Fig. 4. Ellipsoids calculated by U_{ij}(diff.) = U_{ij}(295 K) − U_{ij}(80 K), showing the reduction in thermal motion for each atom upon cooling, are drawn in Fig. 4(*c*). These U_{ij}(diff.) values have been subjected to rigid-body thermal analyses, and results of these calculations are included in Table 6. The *T* values calculated based on U_{ij}(diff.) are in good agreement with the difference between corresponding tensor components calculated at 295 and 80 K. The difference thermal motions in Fig. 4(*c*) are quite reasonable for all atoms except possibly in the case of N(3), where the difference term is quite markedly anisotropic.

We wish to thank Joseph Henriques for his technical assistance.

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The Crystal Structures of 2-Aminophenol and 2-Amino-4-chlorophenol

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Abstract

The crystal structures of 2-aminophenol (I) and 2-amino-4-chlorophenol (II) have been determined from visually estimated Weissenberg data using unfiltered Cu *K* radiation. Crystals of (I) are orthorhombic, space group *Pbca*, with *a* = 7·256 (3), *b* = 7·849 (6), *c* = 19·754 (6) Å. Crystals of (II) are monoclinic, space group $P2_1/c$, with *a* = 11·226 (12), *b* = 7·374 (9), *c* = 8·011 (10) Å, β = 105·8 (3)°. Structure (I) was solved by direct methods and refined by full-matrix least-squares calculations to a final *R* of 11·0% for 693 reflexions; structure (II) was solved by Patterson and electron-density maps and refined by full-matrix least-squares calculations to a final *R* of 10·0% for 807 reflexions. In both structures the molecules are held together by two types of hydrogen bonds forming sheets, and these sheets are held together by weak van

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der Waals contacts. The molecular dimensions are compared with those of related compounds. The C—NH$_2$ lengths and the N-atom deviation from the benzene-ring plane, 1·418 (7) (uncorrected) [1·429 Å (corrected for librational motion)] and 0·115 Å respectively for (I) and 1·427 (9) (uncorrected) [1·433 Å (corrected)] and 0·105 Å respectively for (II), are rather large. From a comparison made with similar structures it is shown that the C—NH$_2$ lengths and the N-atom deviations are linearly related.

Introduction

The crystal-structure analyses of (I) and (II) were undertaken (i) as part of a programme to determine the structures of some aminophenols and their derivatives, (ii) to study the structures of hydrogen-bonded systems, and (iii) to determine the C—OH and C—NH$_2$ lengths which show marked variations in various compounds containing amino and hydroxyl groups. Andersen & Andersen (1975) have shown that C—OH bond lengths are linearly correlated with the acidic strengths (pK_a values). For C—NH$_2$ bonds a correlation has been found to exist between the bond lengths and the deviations of the N atoms from the ring plane. Chao & Schempp (1977) have made similar observations in a recent paper.

Experimental

Crystals of (I) and (II) were grown by slow evaporation of solutions of the substances in acetone and a benzene–acetone mixture respectively. Dark-brown, thick, square-shaped and plate-like crystals of (I) showed prominent cleavage along the *ab* plane and dark-brown plate-like crystals of (II) showed cleavage along the *bc* plane. Axial lengths for both compounds were determined with the help of high-angle reflexions in zero-layer Weissenberg photographs with the films mounted in the Straumanis arrangement. The angle β for (II) was determined by triangulation (Jeffery, 1971). Densities were measured by flotation.

Crystal data

2-Aminophenol (I), C_6H_7NO, M_r = 109; m.p. 447 K; orthorhombic, a = 7·256 (3), b = 7·849 (6), c = 19·754 (6) Å; D_m = 1·283, D_c = 1·289 Mg m^{-3} for Z = 8; $F(000)$ = 464; μ = 0·85 mm^{-1} for Cu $K\alpha$ radiation (λ = 1·5418 Å); space group *Pbca* (No. 61) from systematic absences. Axial lengths and space group agree with the preliminary data reported by Whiteney & Corvin (1949).

2-Amino-4-chlorophenol (II), C_6H_6ClNO, M_r = 143·5; m.p. 411 K; monoclinic, a = 11·226 (12), b = 7·374 (9), c = 8·011 (10) Å, β = 105·8 (3)°; D_m = 1·474, D_c = 1·494 Mg m^{-3} for Z = 4; $F(000)$ = 296; μ = 4·52 mm^{-1} for Cu $K\alpha$ radiation (λ = 1·5418 Å); space group $P2_1/c$ (No. 14) from systematic absences.

The intensity data were collected from Weissenberg photographs; for (I), crystals of dimensions 0·7 × 0·7 × 0·6 and 0·7 × 1·0 × 0·5 mm were used for photographs along the *a* (*hkl*, *h* = 0–4) and *b* (*hkl*, *k* = 0–5) axes respectively; for (II), the crystal dimensions were 0·5 × 0·4 × 0·4 and 0·4 × 0·5 × 0·9 mm for photographs along the *b* (*hkl*, *k* = 0–6) and *c* (*hkl*, *l* = 0–3) axes respectively. Intensities were visually estimated using extended spots in higher-layer photographs and corrected for Lorentz and polarization factors and for spot extensions graphically (*International Tables for X-ray Crystallography*, 1962). Absorption was neglected in both cases. The intensities were put on an absolute scale by a Wilson (1942) plot: for (I) (B = 2·4 Å^2) 699 independent reflexions and for (II) (B = 2·5 Å^2) 811 independent reflexions were obtained.

Structure determination and refinement

2-*Aminophenol*

Initial attempts to solve the structure by trial and error were unsuccessful. A Sayre-equation program* (Long, 1965) was then used with 100 reflexions having $|E| \geq 1{\cdot}2$. Four reflexions (412; 414; 2,1,14; 345) with variable signs were chosen in addition to the three origin-determining ones (4,1,14; 159; 3,2,16). An E map with 100 terms corresponding to the sign set with the highest consistency index (0·90) revealed all the non-hydrogen atoms clearly. Least-squares refinement using the *LALS** program was then started.

The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). Initially, unit weight was given to each reflexion. In the first four cycles of block-diagonal isotropic refinement R fell from 88 to 20%. At this stage a few low-angle reflexions (200, 022, 220, 112, 020 and 040), which had considerably large F_c's as compared with their F_o's, were removed from the refinement. Six more cycles of block-diagonal isotropic refinement brought R down to 16%. Thermal parameters were allowed to become anisotropic and after four block-diagonal cycles R was 14%. Cruickshank's weighting sheme was then introduced: $w = 1/(4{\cdot}4 + |F_o| + 0{\cdot}015|F_o|^2)$, and four full-matrix least-squares cycles reduced R to 11·1%. Finally, two full-matrix cycles including the four ring H atoms, which were located stereochemically, reduced R to 11·0% for 693 reflexions used in the refinement. The H atoms were assumed to have

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* These programs were modified for the CDC 3600-160A computer at the Tata Institute of Fundamental Research, Bombay, by Dr S. S. Tavale of the National Chemical Laboratory, Poona, India.

the same thermal parameters as those of the C atoms to which they are attached; their thermal parameters were not refined. In the final cycle the average shift in the parameters was 0·03σ, the maximum being 0·08σ. An attempt to locate the H atoms of the hydroxyl and amino groups by computing a three-dimensional difference synthesis was unsuccessful.

The final atomic parameters with their estimated standard deviations are given in Table 1.*

2-*Amino*-4-*chlorophenol*

Trial coordinates for the non-hydrogen atoms were obtained from the $P(U0W)$ and $P(UV0)$ sharpened Patterson maps and the corresponding electron-density maps. Refinement of the structure was carried out in the same manner as for (I). A few reflexions (600, 022, 123 and 4̄34), which had considerably large F_c's compared with their F_o's, were removed from the refinement in the later stages. Using Cruickshank's weighting scheme: $w = 1/(4{\cdot}0 + |F_o| + 0{\cdot}030|F_o|^2)$, and including three ring H atoms, gave the final R of 10·0% for the 807 reflexions used in the refinement. In the final cycle, the average shift in the parameters was 0·02σ, the maximum being 0·06σ. The H atoms of the hydroxyl and amino groups could not be located. The final atomic parameters with their estimated standard deviations are given in Table 1.*

Description of the structures and discussion

Crystal packing and hydrogen bonding

Figs. 1 and 2 show the structures of (I) and (II) projected on the (010) and (001) planes respectively.

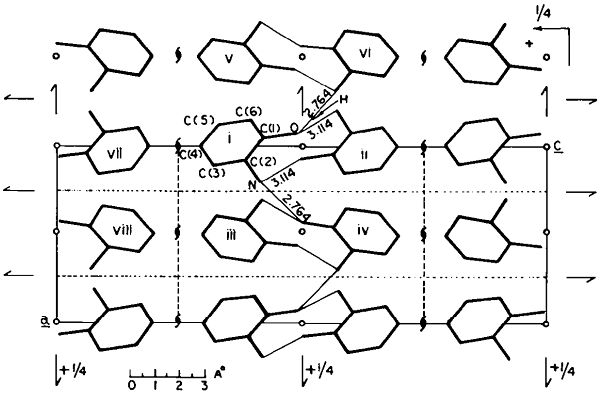

Fig. 1. Crystal structure of 2-aminophenol projected on the (010) plane. Thin solid lines indicate hydrogen bonds. Symmetry codes: (i) x,y,z; (ii) $-x, -y, 1-z$; (iii) $\frac{1}{2}-x, \frac{1}{2}+y, z$; (iv) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; (v) $-\frac{1}{2}-x, \frac{1}{2}+y, z$; (vi) $-\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; (vii) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (viii) $\frac{1}{2}+x, y, \frac{1}{2}-z$.

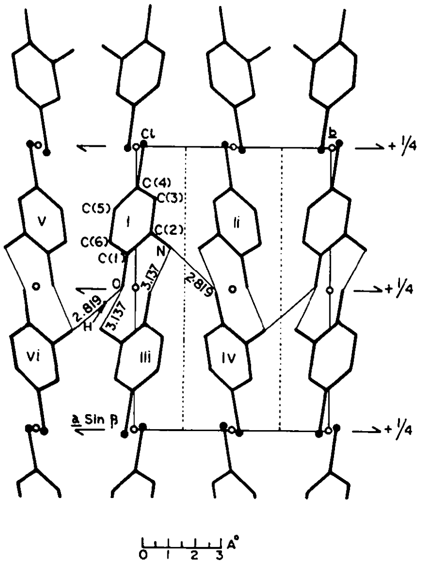

Fig. 2. Crystal structure of 2-amino-4-chlorophenol projected on the (001) plane. Thin solid lines indicate hydrogen bonds. Symmetry codes: (i) x,y,z; (ii) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (iii) $1-x, -y, -z$; (iv) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (v) $x, -\frac{1}{2}-y, \frac{1}{2}+z$; (vi) $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$.

Table 1. *Final atomic parameters* ($\times 10^4$ *for non-hydrogen and* $\times 10^3$ *for* H *atoms*)

E.s.d.'s are given in parentheses and refer to last significant figures.

	x	y	z
2-Aminophenol			
O	−681 (5)	2347 (6)	4967 (2)
N	1941 (7)	835 (7)	4213 (2)
C(1)	−497 (7)	2908 (7)	4315 (3)
C(2)	793 (7)	2078 (7)	3907 (3)
C(3)	1067 (8)	2589 (8)	3245 (3)
C(4)	6 (9)	3943 (9)	2978 (3)
C(5)	−1293 (9)	4747 (9)	3384 (3)
C(6)	−1547 (8)	4216 (9)	4046 (3)
H(3)	208 (7)	194 (9)	296 (9)
H(4)	17 (7)	433 (8)	247 (9)
H(5)	−211 (7)	587 (8)	316 (9)
H(6)	−261 (7)	491 (8)	434 (9)
2-Amino-4-chlorophenol			
Cl	−111 (2)	403 (3)	2763 (3)
O	4981 (4)	−704 (7)	2398 (7)
N	3558 (6)	1770 (8)	285 (8)
C(1)	3798 (6)	−468 (9)	2543 (9)
C(2)	3045 (6)	737 (8)	1426 (9)
C(3)	1845 (6)	1004 (10)	1511 (9)
C(4)	1399 (7)	63 (10)	2712 (10)
C(5)	2150 (7)	−1119 (11)	3857 (10)
C(6)	3353 (7)	−1400 (11)	3760 (11)
H(3)	128 (7)	198 (10)	77 (10)
H(5)	179 (7)	−176 (10)	487 (11)
H(6)	390 (7)	−217 (11)	444 (11)

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34220 (43 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* See previous footnote.

The short intermolecular contacts are between the O and N atoms forming hydrogen bonds. Although the H atoms of the hydroxyl and amino groups could not be located, certain inferences have been drawn on the basis of non-hydrogen-atom positions and knowledge of the molecular geometry. The angle C(6)—C(1)—O [123·1 (5)° in (I) and 122·4 (6)° in (II)] is much larger than C(2)—C(1)—O [117·3 (5)° in (I) and 117·6 (6)° in (II)]. This suggests (Mahmoud & Wallwork, 1975; Andersen & Andersen, 1975) that the H atoms of the OH groups are on the same side of the C(1)—O bonds as C(6), the increase in angle being due to (O)H··· H(6) and (O)H···C(6) repulsions. The expected positions of the OH hydrogens for molecules (i) in (I) and (II) are marked in Figs. 1 and 2 respectively.

In (I), the intermolecular distance between $O(x,y,z)$ and $N(-\frac{1}{2}+x, \frac{1}{2}-y, 1-z)$, 2·764 Å, is most likely an OH···N type hydrogen bond linking the molecules in infinite chains along the a axis. These chains are linked together by two centrosymmetrically related (probably NH···O type) weak hydrogen bonds between $O(x,y,z)$ and $N(\bar{x}, \bar{y}, 1-z)$ and $O(\bar{x}, \bar{y}, 1-z)$ and $N(x,y,z)$, of length 3·114 Å, forming sheets. These sheets are held together by several weak van der Waals contacts between the C atoms. This explains the cleavage of the crystal. The possibility that the second H of the amino group is involved in intramolecular hydrogen bonding appears unlikely. The short N···O intramolecular distance, 2·691 Å, which is shorter than the N···O van der Waals contact (~2·9 Å), is possibly due to intra-molecular and intermolecular steric factors rather than due to a strong hydrogen bond. The small value, ~61°, of the O—N—C(2) angle and the formation of a five-membered ring do not favour intramolecular hydrogen bonding.

The molecular packing in (II) (Fig. 2) is quite similar to that observed in (I). The principal intermolecular contacts are: (i) 2·819 Å between $O(x,y,z)$ and $N(1-x, -\frac{1}{2}+y, \frac{1}{2}-z)$, of the type OH···N, forming chains parallel to the b axis, and (ii) 3·137 Å between $O(x,y,z)$ and $N(1-x, \bar{y}, \bar{z})$ and $O(1-x, \bar{y}, \bar{z})$ and $N(x,y,z)$ forming NH···O type contacts linking the chains to form sheets which are held together by weak van der Waals bonds of lengths 3·574 Å between $Cl(x,y,z)$ and $Cl(\bar{x}, \bar{y}, 1-z)$, and 3·727 Å between $Cl(x,y,z)$ and $Cl(\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z)$. As in (I), the second H atom of the amino group is probably not involved in intramolecular hydrogen bonding.

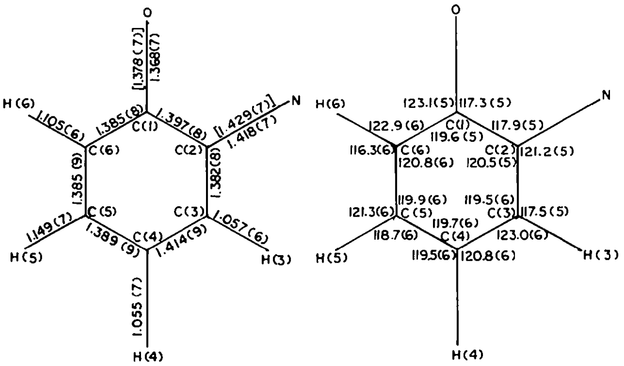

Fig. 3. Bond lengths (Å) (values corrected for molecular libration are in square brackets) and angles (°) in 2-aminophenol. E.s.d.'s are in parentheses.

Molecular structure

Bond lengths and angles for (I) and (II) are given in Figs. 3 and 4 respectively. The equations of the benzene-ring planes for the two compounds referred to the orthogonal axes are given in Table 2 along with the atomic deviations from the respective planes. The benzene rings in (I) and (II) are planar within 0·009 and 0·005 Å respectively. The average C—C length in

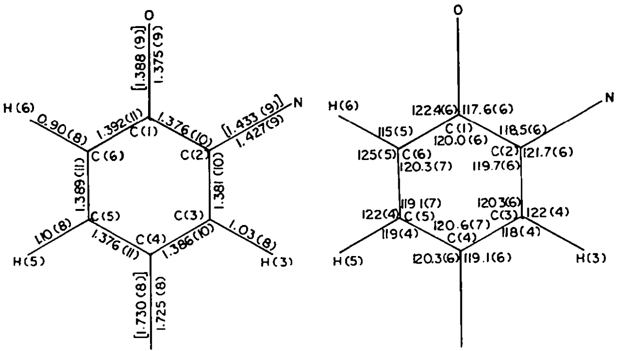

Fig. 4. Bond lengths (Å) (values corrected for molecular libration are in square brackets) and angles (°) in 2-amino-4-chlorophenol. E.s.d.'s are in parentheses.

Table 2. *Deviations* (Å) *of the heavy atoms from the least-squares planes*

2-Aminophenol

Equation of the benzene-ring plane

$$0{\cdot}6947X + 0{\cdot}6537Y + 0{\cdot}3001Z = 3{\cdot}7891$$

C(1)	0·010 (11)	C(6)	−0·007 (13)
C(2)	−0·007 (11)	O†	0·016 (8)
C(3)	0·001 (12)	N†	0·115 (10)
C(4)	0·002 (13)		
C(5)	0·001 (13)		

2-Amino-4-chlorophenol

Equation of the benzene-ring plane referred to the a^*, b, c orthogonal axes

$$0{\cdot}3130X + 0{\cdot}7404Y + 0{\cdot}5948Z = 1{\cdot}5545$$

C(1)	−0·004 (14)	C(6)	−0·003 (16)
C(2)	0·004 (13)	Cl†	−0·035 (4)
C(3)	0·002 (14)	O†	−0·017 (11)
C(4)	−0·009 (15)	N†	0·105 (13)
C(5)	0·009 (16)		

† Atom not included in the plane calculation.

(I), 1·392 Å, is normal, but in (II) it is 1·383 Å, slightly lower than the normal value. From a comparison of the respective C–C lengths in the benzene rings of (I) and (II), it is seen that the C(2)–C(3) [1·382 (8) and 1·381 (10) Å], C(5)–C(6) [1·385 (9) and 1·389 (11) Å] and C(6)–C(1) [1·385 (8) and 1·392 (11) Å] lengths are generally similar. The difference in C(1)–C(2) [1·397 (8) and 1·376 (10) Å] is not significant. The difference in C(3)–C(4) [1·414 (9) and 1·386 (10) Å], which is just at the level of significance (more than 3σ), and that in C(4)–C(5) [1·389 (9) and 1·376 (11) Å], which is not significant (less than even 2σ), are nevertheless as expected. Domenicano, Vaciago & Coulson (1975*a*) have observed that substitution of an electron-withdrawing group for a H atom in a benzene ring results in a shortening of the bonds adjacent to the substituent by 0·01–0·02 Å and an increase in the endocyclic angle α. The C(4)–Cl bond length, 1·725 (8) (uncorrected) [1·730 Å (corrected for librational motion)] and the endocyclic angle α [C(3)–C(4)–C(5)], 120·6 (7)°, agree with the mean C–Cl length [1·740 (1) Å] and angle α [121·4 (1)°] given by Domenicano, Vaciago & Coulson (1975*b*) in Table 9 of their paper.

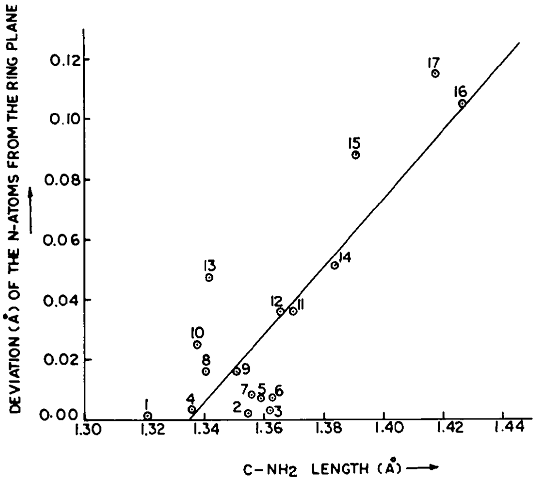

Fig. 5. C–NH_2 lengths *vs* N-atom deviations from the ring plane. (1) 9-Aminoacridine hydrochloride monohydrate (Talacki, Carrell & Glusker, 1974); (2) 2-amino-5-chloropyridine (Kvick & Backeus, 1974); (3) 2:1 complex of 2-aminopyridine with 5,5-diethylbarbituric acid (I-Nan & Craven, 1974); (4) 2-amino-3-nitropyridine (Destro, Pilati & Simonetta, 1975); (5) 2-amino-4-oxo-5-thiazolidineacetic acid (Amirthalingam & Muralidharan, 1972); (6) 4-aminopyridine (Chao & Schempp, 1977); (7) 3-amino-1,4-naphthoquinone (Gaultier & Hauw, 1969); (8) aminopyrazine (Chao, Schempp & Rosenstein, 1976); (9) 2-aminopyridine (Chao, Schempp & Rosenstein, 1975*a*); (10) 2-amino-5-methylpyridine hydrochloride (Sherfinski & Marsh, 1975); (11) *o*-aminobenzoic acid (Brown, 1968); (12) 2-amino-3-chloropyrazine (Morrow & Huddle, 1972); (13) 2-aminopyrimidine (Scheinbeim & Schempp, 1976); (14) 3-aminopyridine (Chao, Schempp & Rosenstein, 1975*b*); (15) 1,2-diaminobenzene monohydrochloride (Stålhandske, 1976); (16) 2-amino-4-chlorophenol (present study); (17) 2-aminophenol (present study).

The C(1)–OH length in (I), 1·368 (7) (uncorrected) [1·378 Å (corrected for librational motion)], agrees well with the C–OH length, 1·375 (9) (uncorrected) [1·388 Å (corrected)], found in (II), and also with the C–OH length, ~1·37 Å, expected on the basis of its pK_a value, 9·66 (Fig. 4 of Kagawa, Kawai, Kashino & Haisa, 1976). The substitution of a Cl atom is not expected to make any significant change in the pK_a value.

The C(2)–NH_2 lengths and N-atom deviations from the benzene-ring planes are: 1·418 (7) (uncorrected) [1·429 Å (corrected)] and 0·115 Å respectively for (I) and 1·427 (9) (uncorrected) [1·433 Å (corrected)] and 0·105 Å respectively for (II). These are large compared with values observed in similar compounds. Fig. 5 shows a plot of the C–NH_2 lengths *vs* N-atom deviations from the ring plane, which clearly indicates a correlation between them. The differences in the C–NH_2 lengths reflect in a general way the degree of double-bond character in the C–N bonds as revealed by the bond lengths. As the conjugation with the ring increases, the C–NH_2 bond length shortens and the amino group acquires nearly *sp*^{2} configuration. On the other hand, as the C–NH_2 length increases the amino group acquires more and more *sp*^{3} character; as a result the amino N deviates from the ring plane. This can be pictorially explained as follows: Fig. 6(*a*), (*b*) and (*c*) shows the molecule viewed along C(4)–C(6) in the benzene plane. If N has *sp*^{2} character, maximum overlap between the ring π electrons and the lone pair of the N atom is possible if N remains in the plane of the ring [Fig. 6(*a*)]. As N acquires some *sp*^{3} character,

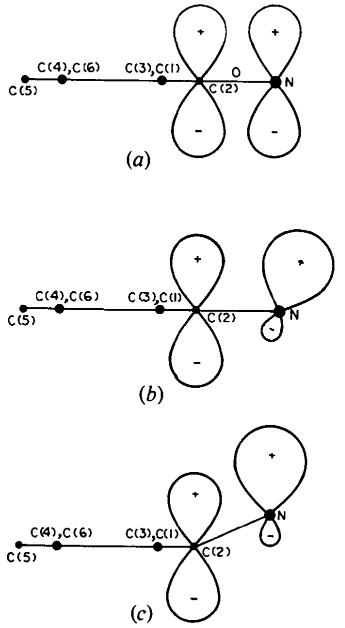

Fig. 6. Schematic picture showing the ring-carbon and the amino-nitrogen atomic orbitals to explain the lengthening of the C–NH_2 bond and the N-atom deviation from the ring plane.

with N in the plane of the ring the lone-pair orbital will approximately be oriented as in Fig. 6(*b*). In order to achieve maximum overlap the N has to deviate from the plane [Fig. 6(*c*)]. In a recent X-ray and NQR study of 4-aminopyridine and related aromatic amines Chao & Schempp (1977) have arrived at a similar conclusion by plotting graphs between: (i) C—N length *vs* dihedral angle, and (ii) C—N length *vs* $360° - \Sigma$, where Σ is the sum of the bond angles around N.

The presence of OH···N-type intermolecular hydrogen bonding can also probably lead to the lengthening of the $C-NH_2$ bond. When a proton migrates to the NH_2 group forming NH_3^+, $C-NH_3^+$ lengths around 1·47 Å are observed. However, in OH···N-type hydrogen bonding, although the proton does not migrate completely to form a covalent bond with N, it could considerably localize the lone-pair electrons along the direction of the hydrogen bond in such a manner as to minimize the possibility of overlap with the orbital of the ring C atom. In (I), $N(x,y,z)$ and $O(\frac{1}{2}+x, \frac{1}{2}-y, 1-z)$ atoms are involved in this type of hydrogen bonding whereas in (II) the corresponding atoms are $N(x,y,z)$ and $O(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$. However, it is hard to decide whether conjugation determines the geometry, which in turn affects the crystal structure, or whether hydrogen bonding is the deciding factor.

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