

Table 4. *Deviations of atoms from least-squares planes*

Atoms with an asterisk are not used to define plane.

Atom	Distance (Å)	Atom	Distance (Å)
Plane A: $0.083x + 8.815y + 5.881z - 2.676 = 0$			
C(1)	0.005 (8)	C(2)	-0.003 (8)
C(3)	-0.006 (8)	C(4)	0.012 (8)
C(5)	-0.009 (8)	C(6)	0.001 (6)
Cl*	0.071 (3)		
Plane B: $10.415x + 8.976y - 1.957z + 1.588 = 0$			
C(12)	-0.012 (6)	C(13)	0.019 (7)
C(14)	-0.008 (8)	C(15)	-0.009 (10)
C(16)	0.015 (11)	C(17)	-0.005 (9)
Plane C: $-0.048x + 8.612y + 5.939z - 2.744 = 0$			
N(2)	-0.008 (6)	C(4)	0.016 (8)
C(5)	-0.016 (8)	C(7)	0.008 (7)
Plane D: $1.339x + 15.804y + 0.642z + 3.591 = 0$			
N(2)	0.045 (6)	C(10)	-0.045 (8)
N(1)	0.047 (6)	C(7)	-0.047 (7)
O*	-0.952 (7)	C(11)	-0.976 (7)
Plane E: $-1.212x - 9.407y + 5.662z - 8.430 = 0$			
N(1)	0.033 (6)	C(8)	-0.060 (9)
C(9)	0.059 (10)	C(10)	-0.031 (8)

Angles between planes (°)

Planes A and B:	85.2 (1.2)
Planes C and D:	127.7 (1.8)
Planes C and E:	69.0 (1.9)
Planes D and E:	121.3 (1.4)

formation and its atomic displacements from the least-squares planes of some parts of the molecule are shown in Table 4. The conformation, bond distances and valence angles of the molecule are in agreement with those found in 8-bromo-1-methyl-6-phenyl-1,2,3,4-tetrahydro-1,5-benzodiazocin-2-one (Andronati, Dvorkin, Simonov, Danilin, Malinovsky & Bogatsky, 1979).

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The Structure of Aniline at 252 K

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Abstract. C₆H₇N, monoclinic, $P2_1/c$, $a = 21.822$ (8), $b = 5.867$ (4), $c = 8.386$ (6) Å, $\beta = 101.01$ (5)°, $V = 1053.9$ (10) Å³, $Z = 8$, $D_x = 1.174$ Mg m⁻³ at 252 K, $M_r = 93.13$, m.p. = 267.18 K. The structure was solved by direct methods and refined by a least-squares

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In the eight-membered ring there is a shortening of the bonds N(2)–C(4) and N(2)–C(10) to 1.41 (2) and 1.38 (2) Å, respectively. A similar effect was noted in studies of the structures of diazepam (Camerman & Camerman, 1972) and medazepam (Gilli, Bertolasi, Sacerdoti & Borea, 1978). This shortening is due to resonance interaction between the amide fragment and the benzo group.

The main difference between the structures of the title compound and its 8-bromo analogue is the orientation of the phenyl ring in position 6. This causes a principal reconstruction of the molecular packing. The distinctive increase in angles at C(8) and C(9) to 116° is probably due to the ring expansion from a seven- to an eight-membered one. The corresponding angle in diazepam is 110.5°. In spite of differences in conformation and some bond distances for the compounds (I) and (II) the projections on the fused benzene ring are similar.

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procedure to an R of 0.063 for 834 reflections. The asymmetric unit contains two crystallographically independent molecules I and II. Both N atoms are out of the benzene plane by about 0.12 Å and the average dihedral angle between the amino (NH₂) plane and the

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benzene plane is $38(3)^\circ$. There are two kinds of $\text{NH}\cdots\text{N}$ hydrogen bonds, with distances of $3.180(6)$ and $3.373(5)$ Å. One hydrogen atom in each amino group is involved in the hydrogen bonding.

Introduction. So far, very few papers have been published on the crystallographic studies of fundamental organic compounds which are liquid at room temperature. This work is part of a series of X-ray studies on the molecular structures and structural properties of organic crystals at a low temperature. Results obtained from the X-ray analysis of aniline in a crystalline state are reported in this paper. A cylindrical crystal 0.5 mm long with a diameter of 0.5 mm was used for the data collection on a Philips PW1100 diffractometer equipped with an NCD-1 low-temperature attachment. The preparation of this crystal was as follows. The temperature stability in the center of the χ circle was first examined and found to be better than 1 K. As shown in Fig. 1, a thin glass capillary with a diameter of 0.5 mm, containing a very small amount of aniline (shaded part), was mounted on a goniometer head. The goniometer head was then set at 90° in the χ circle. When the specimen was blown by the cold and the warm gases from above and the glass capillary was moved very slowly to the left along the φ axis, the crystallization of aniline began at the border of both gases. Because of cracking of the crystal at a temperature below 252 K, the temperature of the cold gas was kept at 252 ± 1 K throughout the experiment. The cell dimensions were obtained by least-squares refinement with 36 reflections. The θ - 2θ scan technique was used to measure the intensities of 2157 reflections up to $2\theta = 50^\circ$ ($\text{Mo K}\alpha$).

The structure was solved by *MULTAN* (Germain, Main & Woolfson, 1971) and all hydrogen atoms were found in the difference Fourier map. By a least-squares procedure, for the 834 reflections having $I > 3\sigma(I)$, R

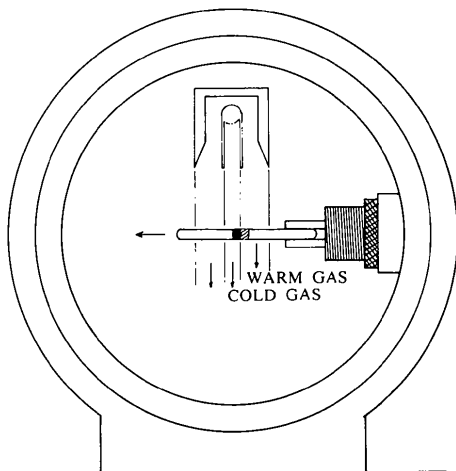


Fig. 1. Crystallization of aniline on a four-circle goniometer.

Table 1. Positional ($\times 10^4$ for non-H atoms and $\times 10^3$ for H atoms) and isotropic thermal parameters

Standard deviations are in parentheses.
For non-H atoms $B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j c \beta_{ij} (\mathbf{a}_i \cdot \mathbf{a}_j)$
($i = j$) $c = 1$, ($i \neq j$) $c = \frac{1}{2}$.

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq} (Å ²)
N(1)	6906 (2)	2484 (7)	6685 (5)	4.7 (1)
C(11)	6532 (2)	3977 (7)	7381 (4)	3.3 (1)
C(12)	5947 (2)	3354 (7)	7642 (5)	3.8 (1)
C(13)	5603 (2)	4751 (8)	8435 (5)	4.2 (1)
C(14)	5833 (2)	6861 (8)	9029 (6)	4.5 (1)
C(15)	6417 (2)	7500 (8)	8763 (5)	4.2 (1)
C(16)	6767 (2)	6111 (8)	7957 (5)	3.6 (1)
N(2)	8076 (2)	2132 (6)	-52 (4)	3.9 (1)
C(21)	8447 (2)	3669 (7)	954 (5)	3.3 (1)
C(22)	9047 (2)	3103 (8)	1737 (5)	3.8 (1)
C(23)	9393 (2)	4562 (8)	2845 (6)	4.3 (1)
C(24)	9151 (2)	6640 (8)	3199 (6)	4.5 (1)
C(25)	8567 (2)	7250 (8)	2415 (5)	4.0 (1)
C(26)	8208 (2)	5797 (8)	1304 (5)	3.8 (1)

	<i>x</i>	<i>y</i>	<i>z</i>	B_{iso} (Å ²)
H(N1A)	731 (2)	300 (8)	623 (5)	5.5 (12)
H(N1B)	661 (3)	154 (10)	602 (7)	8.6 (15)
H(C12)	585 (2)	196 (7)	731 (5)	4.8 (11)
H(C13)	515 (2)	436 (9)	862 (5)	6.1 (12)
H(C14)	555 (2)	792 (8)	959 (5)	5.3 (11)
H(C15)	658 (2)	891 (7)	918 (5)	4.1 (10)
H(C16)	719 (2)	646 (6)	768 (4)	2.3 (8)
H(N2A)	773 (1)	267 (6)	-93 (4)	2.3 (8)
H(N2B)	826 (2)	128 (9)	-47 (6)	7.1 (14)
H(C22)	926 (2)	186 (8)	161 (5)	4.7 (11)
H(C23)	977 (2)	414 (6)	342 (4)	2.8 (8)
H(C24)	939 (2)	762 (9)	403 (6)	6.9 (13)
H(C25)	836 (2)	882 (9)	274 (5)	5.8 (12)
H(C26)	775 (2)	616 (9)	64 (6)	6.6 (13)

These values correspond to molecules I and II in Fig. 5.

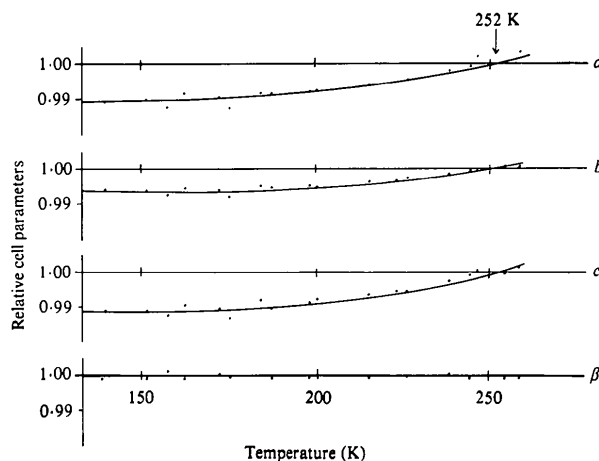


Fig. 2. Temperature dependence of the cell parameters.

was reduced to 0.063. The atomic scattering factors of Cromer & Waber (1974) were used for C and N atoms, and those of Stewart, Davidson & Simpson (1965) for H. The atomic coordinates are given in Table 1.* Fig. 2 shows the temperature dependence of the cell parameters.

Discussion. Structures of the independent molecules I and II, with atomic numbering scheme, bond lengths and angles, are shown in Fig. 3. If the e.s.d.'s are taken into account, the molecular structure of I is nearly identical with that of II. As can be seen in Fig. 4, the N atoms of both molecules are out of the benzene plane by 0.113 (4) (molecule I) and 0.122 (3) Å (molecule II). H atoms of each amino group are found to be out of the benzene plane in the opposite direction to that of the N atom: H(N1A) 0.09 (4), H(N1B) 0.27 (5), H(N2A) 0.23 (3), H(N2B) 0.19 (5) Å. In each of the molecules, the N atom deviates from the H(NA)—H(NB)— α -C plane by 0.25 (3) (I) and 0.28 (3) Å (II). The dihedral angle (ψ) between the amino (NH_2) plane and the benzene plane is 37 (4)° in molecule I and 38 (4)° in molecule II, compared with 37.5 (20) and 47.7° based on the microwave spectrum (MW) (Lister & Tyler, 1974) and the molecular orbital calculation (MO) (Hehre, Radom & Pople, 1972*a,b*), respectively. The sum ($\sum \nu$) of bond angles (ν) around the N atom is 346 (11)° for molecule I, and 338 (11)° for molecule II. They are intermediate between those for sp^2 (360°) and sp^3 (328.4°) hybridized N atoms, and close to the sum (348°) found in *p*-thiocyanatoaniline (Isakov, Rider & Zvonkova, 1977),

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36308 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

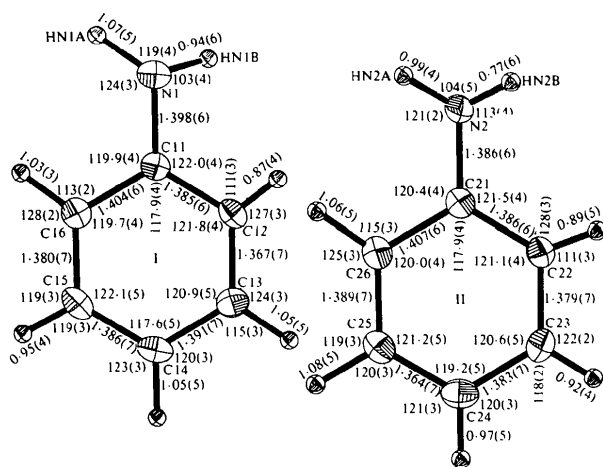


Fig. 3. Structures of the independent molecules I and II with bond lengths (Å) and angles (°).

whereas those in both *o*-nitroaniline (Dhaneshwar, Tavale & Pant, 1978) and trinitroaniline (Holden, Dickinson & Bock, 1972) are 360°. The C—N bond distances are 1.398 (6) (I) and 1.386 (6) Å (II), which agree with that estimated by MW measurement [1.402 (2) Å] (Lister & Tyler, 1974), and are also compatible with the correlation between C—N bond lengths in primary aromatic amines and the average length of C—C bonds in the benzene ring (Holden, Dickinson & Bock, 1972). As Fig. 5 shows, the molecules are linked by two kinds of weak hydrogen bond, N(1)—H(N1A)···N(2) and N(2)—H(N2A)···N(1), with distances of 3.180 (6) [H(N1A)···N(2) 2.16 (5)] and 3.373 (5) Å [H(N2A)···N(1) 2.43 (3) Å], in the (100) plane, and the angles around the H atoms are 159 (4) and 158 (3)°, respectively. Thus, the N(1) atom is out of the benzene plane toward the H(N2A) atom in a neighbor molecule, and the N(2) atom toward the H(N1A). The H(N1B) and H(N2B) atoms are free from hydrogen bonding.

The conformations of the amino group in aniline and substituted anilines are as follows. (i) According to structural studies of aniline (MW, Lister & Tyler, 1974; MO, Hehre, Radom & Pople, 1972*a,b*) and *p*-substituted anilines ($X-\text{C}_6\text{H}_5\text{NH}_2$; $X = \text{NO}_2, \text{CH}_3$,

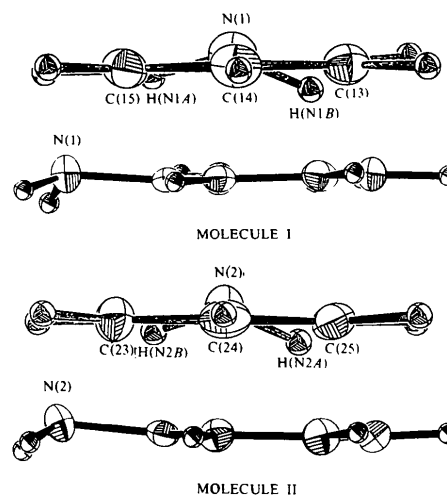


Fig. 4. Perspective view of the molecules I and II.

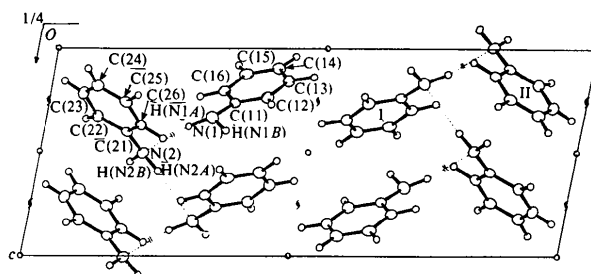


Fig. 5. The crystal structure viewed along the *b* axis showing intermolecular hydrogen bonds.

F, OH, NH₂) (MO, Hehre, Radom & Pople, 1972*a, b*), a N atom in an isolated molecule lies on the same plane as the plane of the benzene ring. The HNH plane is bent out of its plane. The CNH₂ group has a pyramidal shape. The angle ψ is 47.7° (MO) and 37.5° (MW) for aniline and 44.3° (MO) for *p*-nitroaniline (Hehre, Radom & Pople, 1972*a, b*). (ii) When both hydrogen atoms of the amino group in the substituted anilines (e.g. *p*-nitroaniline and trinitroaniline) (Trueblood, 1961; Holden, Dickinson & Bock, 1972) form hydrogen bonds (NH...O), the HNH plane in each molecule is coplanar with the benzene ring. Then, the geometry around N is trigonal planar. The trigonal plane of *p*-nitroaniline (Trueblood, 1961) is slightly twisted around the C—N bond. In the case of *m*-nitroaniline (Skapski & Stevenson, 1973) and the complex of pentachlorophenol and aniline (Van Bellingen, Germain, Piret & Van Meerssche, 1971), each hydrogen atom of the amino group forms a hydrogen bond and each N atom remains coplanar with its benzene ring. Although *N,N*-diethyl-*p*-nitrosoaniline (Talberg, 1977) has no hydrogen bond, its C(Et)NC(Et) group and its benzene ring share the same plane. The geometry of the amino N in *o*-nitroaniline (Dhaneshwar, Tavale & Pant, 1978) is also trigonal planar. (iii) In *p*-thiocyanatoaniline (Isakov, Rider & Zvonkova, 1977), the two hydrogen atoms form hydrogen bonds as usual, but the amino N atom acts as a proton acceptor. This causes the amino N atom to deviate slightly (0.055 Å) from its benzene plane. The value $\sum \nu$ is 348° and the geometry around the N atom is pyramidal. (iv) X-ray studies of the present crystal and the complex of 2,4,5-trichlorophenol and aniline (ATCP) (Van Bellingen, Germain, Piret & Van Meerssche, 1971) show interesting results. One of the two amino hydrogen atoms in each aniline molecule is involved in a hydro-

gen bond. Each N atom works as proton acceptor and each one deviates greatly from its benzene plane (aniline 0.113, 0.112; ATCP 0.135 Å). $\sum \nu$ is 346 and 338° in aniline, and 346° in ATCP. N atoms in these compounds are thus pyramidal.

We wish to express our thanks to Dr T. Kamikawa of this University for the specimen purification.

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Nouvel Affinement de la Structure de l'Acide Dodécanedioïque*

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(Reçu le 20 mars 1981, accepté le 20 juillet 1981)

Abstract. C₁₂H₂₂O₄, $M_r = 230.30$, $P2_1/c$, $Z = 2$, $a = 13.105$ (7), $b = 4.921$ (2), $c = 10.183$ (3) Å, $\beta = 97.40$ (3)°, $V = 651.2$ (8) Å³, $F(000) = 252$, $d_o = 1.19$, $d_c = 1.17$ Mg m⁻³. The structure which had been previously solved [Housty & Hospital (1966), *Acta Cryst.* 21, 553–559] has been refined by full matrix least squares to a final R of 0.036 for 548 reflections. The

molecules are aligned in the ab plane in the [110] direction and form infinite chains through hydrogen bonding characterized by O(1)—H(O1) = 0.97 (3) Å, H(O1)...O(2'') = 1.70 (3) Å, O(1)...O(2'') = 2.654 (3) Å and O(1)—H(O1)...O(2'') = 172 (3)°.

Introduction. Au cours de notre programme d'étude des composés à longues chaînes aliphatiques nous avons synthétisé les sels de pipérazinium des acides

* Etude des Composés à Chaînes Aliphatiques. 5.