

**Discussion.** The structure confirms a *trans* configuration of the 1 and 4 substituents and shows that both are pseudo-axial. The only significant intermolecular contact is a hydrogen bond between H(16) and O(11'), the latter in the molecule at  $x - 1, y, z$ . The H(16)···O(11') distance is 2.17 (3) Å; the O(16)–H(16)–O(11') angle is 168 (1)°.

The geometry of the 3,4,5-trimethoxyphenethyl substituent was compared to those found in this same fragment in other molecules by use of the Cambridge Crystallographic Database search and geometry calculation systems (Allen *et al.*, 1979). The arrangement of the three adjacent methoxy groups in this substituent is typical. The 3' and 5' groups are nearly coplanar with the benzene ring: the plane of the former [C(3'), O(7'), C(8')] makes an angle of 5.2 (8)° with the mean plane of the benzene ring [C(1')–C(6')]; that of the latter [C(5'), O(11'), C(12')] makes an angle of 1.8 (8)° (see also Table 4). The plane of the 4' group [C(4'), O(9'), C(10')] makes an angle of 99.4 (8)° with the benzene mean plane. The C–O–CH<sub>3</sub> bond angles in the 3' and 5' groups, 119.1 (3) and 117.2 (3)°,

respectively, are significantly larger than the corresponding angle in the 4' group, 112.1 (3)°. This is the result of steric interaction with the ring protons at positions 2' and 6' respectively. The geometry of the methoxy group at the 6 position of the isoquinoline is similar to those of the 3' and 5' groups: the group is nearly coplanar with the aromatic ring C(4a)–C(8a) [the angle is 5.1 (8)°; see also Table 4] and the C–O–CH<sub>3</sub> angle is 117.0 (3)°.

The plane of atoms C(7), O(19), C(20) and C(22) is perpendicular to that of the aromatic ring C(4a)–C(8a). The phenyl ring C(22)–C(27) makes an angle of 27.0 (8)° with this aromatic ring. The pattern of thermal parameters for the atoms in this phenyl ring is unusual and not readily interpretable in terms of any imagined thermal motion of the ring. Refinement of the ring as a rigid body did not improve the thermal parameters.

We thank the Science Research Council for financial support. Calculations were performed on the University of Cambridge IBM 370/165 computer with *SHELX* 76 (Sheldrick, 1976).

Table 4. Deviations (Å) of atoms from mean planes

| Average e.s.d. is 0.005 Å.               |        |        |        |
|--|--------|--------|--------|
| (a) Mean plane through atoms C(1')–C(6') |        |        |        |
| C(1')                                    | 0.014  | O(7')  | 0.007  |
| C(2')                                    | –0.008 | C(8')  | –0.096 |
| C(3')                                    | –0.006 | O(9')  | 0.042  |
| C(4')                                    | 0.014  | O(11') | –0.034 |
| C(5')                                    | –0.008 | C(12') | –0.014 |
| C(6')                                    | –0.006 |        |        |
| (b) Mean plane through atoms C(4a)–C(8a) |        |        |        |
| C(4a)                                    | –0.007 | C(8)   | 0.005  |
| C(5)                                     | 0.006  | C(8a)  | 0.002  |
| C(6)                                     | 0.001  | O(17)  | –0.026 |
| C(7)                                     | –0.006 | C(18)  | 0.008  |

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*Acta Cryst.* (1982). **B38**, 671–673

## Structure of *p*-Nitroaniline Hydrochloride

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(Received 18 March 1981; accepted 7 August 1981)

**Abstract.** C<sub>6</sub>H<sub>7</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup>.Cl<sup>–</sup>, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 4.9794 (5), *b* = 16.331 (2), *c* = 10.282 (1) Å, β = 115.01 (1)°, *Z* = 4, *D*<sub>m</sub> = 1.519, *D*<sub>x</sub> = 1.530 Mg m<sup>–3</sup>, λ(Cu *K*α<sub>1</sub>) = 1.54051 Å, λ(Mo *K*α) = 0.7107 Å, μ(Mo *K*α) = 46 mm<sup>–1</sup>, *F*(000) = 360. The structure of *p*-nitroaniline hydrochloride was determined from

diffractometer data; final *R* = 0.073 for 1477 reflexions. The molecular structures of *p*-nitroaniline and *p*-nitroaniline hydrochloride are compared.

**Introduction.** Crystals of *p*-nitroaniline hydrochloride were obtained by the addition of gaseous hydrogen

chloride to a solution of *p*-nitroaniline in ether. The product was recrystallized from a mixture of ethanol and concentrated hydrochloric acid and dried, first over potassium hydroxide and then over phosphorus pentoxide. The formula weight was determined by titration with sodium hydroxide solution to be 176 (theoretical value 174.59). The lattice constants were determined from quartz-calibrated Guinier-Hagg diagrams (Cu  $K\alpha_1$  radiation) by least-squares calculations.

The systematically extinct reflexions ( $h0l$  with  $l$  odd,  $0k0$  with  $k$  odd) indicated space group  $P2_1/c$ . The data collection was performed on an automatic diffractometer using graphite-monochromatized Mo  $K\alpha$  radiation. The intensity was recorded during an  $\omega$  scan of  $2.0^\circ$ , at a scan speed of  $0.62^\circ \text{ min}^{-1}$  and for half the scan-time at each end of the scanning interval. The reflexion 063 was remeasured after every 10 reflexions. These measurements provided material for calculating corrections for a linear fall-off of intensities with time. All reflexions  $hkl$  and  $hk\bar{l}$  in the range  $2.5^\circ < \theta < 30^\circ$  were measured. The intensities were corrected for Lorentz and polarization effects, but no correction for absorption or extinction was made. In the  $\theta$  range  $2.5\text{--}30^\circ$  there are 1725 unique reflexions of which 1477 having  $F^2 > 2.5\sigma(F^2)$  were used in the structure determination and structure refinement.

The structure was determined by direct methods using programs included in the XRAY system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). The solution was obtained with the programs *NORMSF*, *SINGEN*, *PHASE*, *FOURR*, *PEKPIK* and *BUILDM*. One trial gave coordinates for all non-hydrogen atoms. The structure was refined by least-squares calculations with the program *CRYLSQ*. In the first few cycles of refinement positional parameters and individual isotropic temperature factors were varied. Positions of the seven H atoms were found at this stage in difference electron density maps. In the final cycles of refinement positional parameters for all

atoms and anisotropic temperature parameters for Cl, O, N and C atoms were allowed to vary.

The quantity minimized was  $\sum w(F_o - F_c)^2$ . The weighting scheme was  $w = (a + F_o + bF_o^2)^{-1}$ . With  $a = 12.0$  and  $b = 0.06$  the mean values of  $w(F_o - F_c)^2$  were almost independent of  $\sin \theta$  and the magnitudes of  $F_o$ . Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The refinement resulted in  $R = \sum |F_o| - |F_c| / \sum |F_o| = 0.073$  and  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.095$ . The final parameters are given in Table 1.\*

**Discussion.** The contents of one unit cell are shown in Fig. 1. The crystal structure is composed of layers of anilinium ions perpendicular to the  $a$  axis. These layers are held together by ionic forces and hydrogen bonds. The  $-\text{NH}_3^+$  group is a donor in three hydrogen bonds, in which chloride ions are acceptors. The average distance between the N atom and the accepting chloride ions,  $3.19 \text{ \AA}$ , is exactly as found by Fuller (1959). The distances between the chloride ion and surrounding N and O atoms and the distances between N in the  $-\text{NH}_3^+$  group and O in the nitro group are shown in Fig. 1.

Details of the molecular structure of *p*-nitroaniline hydrochloride are given in Tables 2 and 3. From Table 2 it is concluded that the aromatic ring is planar and that N(2) lies in the plane defined by C(4), O(1) and O(2). The nitro group is bent out of the ring plane and

Table 1. Final atomic coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors ( $\text{\AA}^2$ ) with e.s.d.'s in parentheses

$$B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j b_{ij} (\mathbf{a}_i \cdot \mathbf{a}_j).$$

|       | $x$       | $y$      | $z$      | $B_{\text{eq}}$ |
|-------|-----------|----------|----------|-----------------|
| Cl(1) | 944 (2)   | 3113 (1) | 788 (1)  | 3.08 (5)        |
| C(1)  | -3019 (8) | 6265 (2) | 1920 (4) | 2.63 (16)       |
| C(2)  | -4949 (8) | 5611 (3) | 1487 (5) | 3.18 (17)       |
| C(3)  | -3958 (9) | 4845 (3) | 2050 (5) | 3.18 (17)       |
| C(4)  | -1040 (9) | 4762 (3) | 3014 (4) | 2.89 (16)       |
| C(5)  | 898 (8)   | 5410 (3) | 3455 (5) | 3.18 (17)       |
| C(6)  | -109 (9)  | 6177 (3) | 2902 (5) | 3.31 (18)       |
| N(1)  | -4025 (7) | 7082 (2) | 1302 (4) | 3.03 (14)       |
| N(2)  | 52 (8)    | 3936 (2) | 3578 (4) | 3.29 (16)       |
| O(1)  | -1724 (8) | 3380 (2) | 3280 (4) | 4.88 (18)       |
| O(2)  | 2708 (7)  | 3854 (2) | 4319 (4) | 4.38 (16)       |

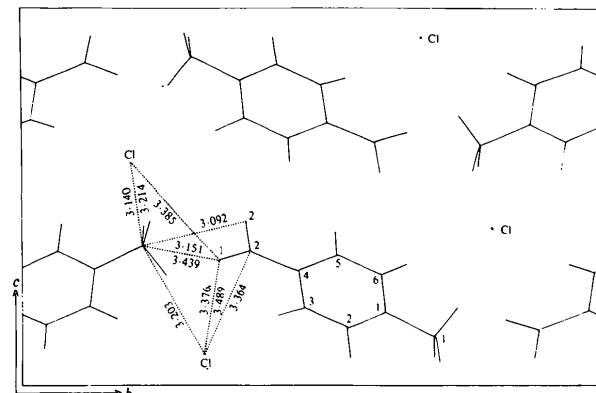


Fig. 1. The structure viewed down the  $a$  axis. The estimated standard deviations of the contact distances are in the range  $0.003\text{--}0.006 \text{ \AA}$ .

\* Lists of structure factors and anisotropic temperature parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36350 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Deviations (Å) of atoms from planes through the *p*-nitroanilinium ion

The mean e.s.d. on the deviations of the heavy atoms is 0.004 Å.

Equations of planes

$$(I) -3.17758X + 2.92726Y + 9.75111Z = 4.66828$$

$$(II) -2.68432X + 3.24166Y + 9.97052Z = 4.82825$$

(a) Atoms defining the planes

|      | (I)    | (II) |
|------|--------|------|
| C(1) | -0.003 | C(4) |
| C(2) | -0.003 | O(1) |
| C(3) | 0.006  | O(2) |
| C(4) | -0.005 |      |
| C(5) | -0.001 |      |
| C(6) | 0.005  |      |

(b) Atoms not included in defining the planes

|      | (I)    | (II)       |
|------|--------|------------|
| N(1) | -0.047 | N(2) 0.001 |
| N(2) | -0.044 |            |
| O(1) | 0.067  |            |
| O(2) | -0.190 |            |

The angle between plane (I) and plane (II) is 7.0 (0.5)°.

twisted around the C(4)–N(2) bond (dihedral angle between the ring plane and the nitro group 7.0°). The structure of *p*-nitroaniline was determined by Trueblood, Goldish & Donohue (1961). They described the structure as being *p*-quinonoidal. In Table 3 the bond lengths and bond angles in the amine hydrochloride are compared with the bond lengths and bond angles in the amine. The average C–C distance in the amine hydrochloride is 1.378 Å and the average C–C distance in the amine is 1.393 Å. In *p*-nitroaniline hydrochloride the lengths of the C–C bonds deviate insignificantly from the average C–C bond. The C(1)–N(1) and C(4)–N(2) bonds are longer in *p*-nitroaniline hydrochloride than in *p*-nitroaniline. The quinonoid structure found in *p*-nitroaniline is not present in the hydrochloride.

Table 3. Bond lengths (Å) and angles (°) involving non-hydrogen atoms, with e.s.d.'s in parentheses

(I) In *p*-nitroaniline hydrochloride.  
(II) In *p*-nitroaniline (Trueblood, Goldish & Donohue, 1961).

|                | (I)*      | (II)*     |
|----------------|-----------|-----------|
| C(1)–C(2)      | 1.379 (6) | 1.408 (6) |
| C(2)–C(3)      | 1.379 (6) | 1.377 (7) |
| C(3)–C(4)      | 1.376 (5) | 1.390 (6) |
| C(4)–C(5)      | 1.374 (6) | 1.395 (6) |
| C(5)–C(6)      | 1.379 (6) | 1.373 (7) |
| C(6)–C(1)      | 1.379 (5) | 1.415 (7) |
| C(1)–N(1)      | 1.472 (5) | 1.371 (7) |
| C(4)–N(2)      | 1.478 (5) | 1.460 (7) |
| N(2)–O(1)      | 1.213 (5) | 1.246 (7) |
| N(2)–O(2)      | 1.223 (5) | 1.247 (7) |
| C(6)–C(1)–C(2) | 121.9 (4) | 118.9†    |
| C(2)–C(1)–N(1) | 120.0 (3) | 121.2     |
| C(6)–C(1)–N(1) | 118.1 (3) | 119.9     |
| C(1)–C(2)–C(3) | 119.4 (3) | 120.8     |
| C(2)–C(3)–C(4) | 118.2 (4) | 119.2     |
| C(3)–C(4)–C(5) | 122.8 (4) | 121.2     |
| C(3)–C(4)–N(2) | 118.3 (4) | 120.4     |
| C(5)–C(4)–N(2) | 118.9 (3) | 118.4     |
| C(4)–C(5)–C(6) | 118.8 (3) | 119.8     |
| C(5)–C(6)–C(1) | 118.9 (4) | 120.1     |
| C(4)–N(2)–O(1) | 118.4 (3) | 117.7     |
| C(4)–N(2)–O(2) | 117.8 (4) | 119.0     |
| O(1)–N(2)–O(2) | 123.8 (4) | 123.3     |

\* The values for *p*-nitroaniline are corrected for thermal vibrations, while the values for the hydrochloride are uncorrected.

† The standard deviations of the bond angles at C atoms are about 0.4°, those at N about 0.35°.

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