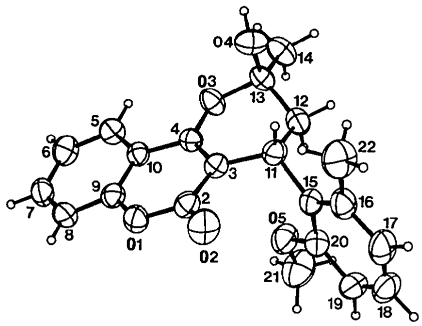


Fig. 4. An ellipsoid plot of (4).

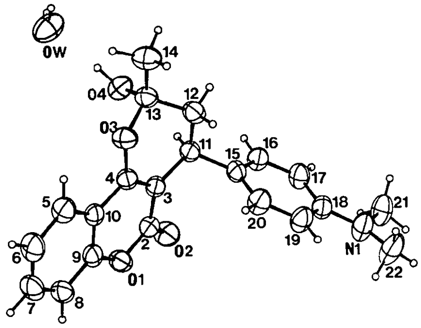
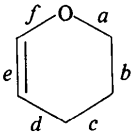


Fig. 5. An ellipsoid plot of (5).

A 3,4-dihydro-2*H*-pyran ring is embedded in each structure. The unsaturation is part of the coumarin ring and other ring substituents are 2-methyl, 2-hydroxyl or methoxyl, and 4-aryl. Rings in both (1) and (2) are half chairs strongly distorted toward the *d*,*e*-diplanar forms, (3)–(5) are essentially half-chairs. Intraring torsion angles are given in Table 7.

Table 7. *Torsion angles* (°) *in the dihydropyran rings*

E.s.d.'s are at most about 0·5°; common configuration.



	a	*b*	*c*	*d*	*e*	*f*
(1)	–50·2	59·5	–36·6	5·7	3·5	20·0
(2)	–51·9	60·4	–35·3	2·0	6·3	20·1
(3)	–45·2	60·3	–42·9	10·7	4·6	13·9
(4)	–42·1	59·3	–45·4	15·2	1·4	12·8
(5)	–44·3	63·6	–48·3	16·0	3·6	11·3

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Structure Redetermination of *m*-Nitroaniline and Structure Determination of *m*-Nitroaniline Hydrochloride

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Abstract. *m*-Nitroaniline, $C_6H_6N_2O_2$: $M_r = 138{\cdot}1$, orthorhombic, $Pbc2_1$, $a = 6{\cdot}499$ (1), $b = 19{\cdot}369$ (4), $c = 5{\cdot}084$ (1) Å, $V = 639{\cdot}9$ (4) Å^3, $Z = 4$, $D_m = 1{\cdot}430$(1) by flotation, $D_x = 1{\cdot}434$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 12$ mm^{-1}, $F(000) = 288$, $T = 295$ K. $R = 0{\cdot}037$ for 769 reflexions. The *m*-nitroaniline molecules are held together by van der Waals forces. The benzene ring is planar; the two N atoms are out of

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this plane in opposite directions [N(1) by 0·05 (0·005), N(2) by −0·01 (0·005) Å]. *m*-Nitroaniline hydrochloride, $C_6H_7N_2O_2^+.Cl^-$: $M_r = 174\cdot6$, monoclinic, $P2_1/c$, $a = 9\cdot476\ (1)$, $b = 9\cdot732\ (1)$, $c = 8\cdot459\ (1)$ Å, $\beta = 78\cdot76\ (1)^\circ$, $V = 765\cdot1\ (3)$ Å^3, $Z = 4$, $D_m = 1\cdot513(1)$ by flotation, $D_x = 1\cdot516$ Mg m^{-3}, $\lambda(\mathrm{Mo}\,K\alpha) = 0\cdot71069$ Å, $\mu = 45$ mm^{-1}, $F(000) = 360$, $T = 295$ K. $R = 0\cdot031$ for 2019 reflexions. The structure is held together by ionic and hydrogen bonds (average N···Cl$^-$ distance is 3·171 Å). The benzene ring is planar; the two N atoms are out of this plane in opposite directions [N(1) by 0·01 (0·002), N(2) by −0·05 (0·002) Å].

Introduction. As part of a programme of structure determinations of substituted anilines and substituted aniline hydrochlorides the structures of *m*-nitroaniline and *m*-nitroaniline hydrochloride are reported. The aim of the programme is to determine the changes in molecular structure of anilines on protonation. The structure of *m*-nitroaniline was determined by Skapski & Stevenson (1973). In this determination the lengths of the C—C bonds deviate significantly from the average C—C bond [C(1)—C(6) 1·419 Å, C(4)—C(5) 1·348 Å, mean C—C bond length 1·384 Å].

Experimental. *m*-Nitroaniline was recrystallized from acetone. Yellow needles cut to 0·15 × 0·57 × 0·33 mm, Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized, pulse-height-discriminated Mo$K\alpha$, lattice parameters from Guinier–Hägg photographs with Cu$K\alpha_1$ ($\lambda = 1\cdot54051$ Å) and quartz as internal standard, 1018 unique reflexions ($0 \leq h \leq 9, 0 \leq k \leq 26, 0 \leq l \leq 7$) with $2\cdot5 < \theta < 30^\circ$, 769 with $I > 2\cdot5\sigma(I)$, $\omega/2\theta$ scan, standard reflexion 361 (max. correction for decrease 13%), systematic absences $0kl$ with k odd, $h0l$ with l odd, Lp correction, absorption ignored, atomic coordinates from previous determination (Skapski & Stevenson, 1973). Origin of 2_1 axis fixed by invariant z coordinate of O(1) [zO(1) = −0·0050], no determination of absolute configuration, full-matrix least-squares refinement; non-H anisotropic, H fixed thermal parameters, $\sum w(\Delta|F|)^2$ minimized, final $R = 0\cdot037$ and $wR = 0\cdot047$, weights $w = 1/(4\cdot0 + |F_o| + 0\cdot027|F_o|^2)$ gave average $w\Delta(|F|)^2$ independent of $\sin\theta$ and $|F_o|$; $S = 0\cdot847$. $(\Delta/\sigma)_{\max} = 0\cdot06$; maximum and minimum values of electron density in final difference map: 0·16 and −0·15 e Å^{-3}; scattering factors from *International Tables for X-ray Crystallography* (1962), computer programs from *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).

Table 1. *Final atomic coordinates for m-nitroaniline with standard deviations* (×10^4) *and equivalent isotropic temperature factors* (Å^2)

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j b_{ij}(\mathbf{a}_i.\mathbf{a}_j).$$

	x	y	z	B_{eq}
C(1)	5419 (3)	1512 (1)	5426 (8)	3·61 (15)
C(2)	3953 (3)	1674 (1)	3533 (8)	3·57 (15)
C(3)	2281 (3)	1236 (1)	3240 (8)	3·45 (15)
C(4)	1986 (4)	648 (1)	4702 (8)	4·12 (17)
C(5)	3457 (4)	497 (1)	6589 (8)	4·61 (20)
C(6)	5151 (4)	919 (1)	6945 (7)	4·10 (18)
N(1)	7072 (3)	1955 (1)	5852 (8)	4·66 (17)
N(2)	756 (3)	1411 (1)	1220 (7)	4·32 (15)
O(1)	951 (3)	1942 (1)	−50	6·09 (19)
O(2)	−667 (3)	1010 (1)	855 (8)	6·79 (22)

Table 2. *Final atomic coordinates for m-nitroaniline hydrochloride with standard deviations* (×10^4) *and equivalent isotropic temperature factors* (Å^2)

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j b_{ij}(\mathbf{a}_i.\mathbf{a}_j).$$

	x	y	z	B_{eq}
Cl	8301 (1)	4340 (1)	2272 (1)	2·61 (2)
C(1)	7891 (1)	779 (1)	2976 (1)	2·18 (7)
C(2)	8262 (1)	−186 (1)	1777 (1)	2·17 (7)
C(3)	7152 (1)	−788 (1)	1182 (1)	2·22 (7)
C(4)	5724 (1)	−459 (1)	1726 (2)	2·74 (8)
C(5)	5397 (1)	519 (2)	2932 (2)	3·10 (9)
C(6)	6476 (1)	1138 (1)	3567 (2)	2·81 (8)
N(1)	9031 (1)	1447 (1)	3633 (1)	2·52 (7)
N(2)	7524 (1)	−1854 (1)	−52 (1)	2·87 (7)
O(1)	8792 (1)	−2201 (1)	−439 (1)	4·12 (9)
O(2)	6555 (1)	−2339 (1)	−639 (1)	4·47 (9)

The experimental conditions for *m*-nitroaniline hydrochloride were as above except: crystals were obtained by adding gaseous hydrogen chloride to a solution of *m*-nitroaniline in ether. The product was recrystallized from a mixture of ethanol and concentrated hydrochloric acid, then dried in a desiccator, first over potassium hydroxide and then over phosphorus pentoxide. The formula weight was determined to be 176 (theoretical value 174·6) by titration with 0·1M sodium hydroxide. Colourless prisms 0·44 × 0·39 × 0·29 mm, 2305 unique reflexions ($0 \leq h \leq 13, 0 \leq k \leq 13, -11 \leq l \leq 11$) with $2\cdot0 < \theta < 30^\circ$, 2019 with $I > 2\cdot5\sigma(I)$, standard reflexion 502 stable, systematic absences $h0l$ with l odd, $0k0$ with k odd, direct methods, hydrogen-atom positions from difference Fourier map calculated when $R = 0\cdot091$ (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). Final $R = 0\cdot031$, $wR = 0\cdot044$, $w = 1/(2\cdot6 + |F_o| + 0\cdot022|F_o|^2)$. $S = 1\cdot023$, $(\Delta/\sigma)_{\max} = 0\cdot009$; maximum and minimum values of electron density in final difference map: 0·25 and −0·32 e Å^{-3}.

Discussion. Final atomic coordinates and equivalent isotropic temperature factors are given in Tables 1 and 2.* The contents of the unit cells are shown in Figs. 1

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* Lists of structure factors, anisotropic temperature parameters, H-atom parameters and deviations of atoms from least-squares planes through the carbon rings and the nitro groups have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43207 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

and 2. The crystal structure of *m*-nitroaniline was described by Skapski & Stevenson (1973). The shortest intermolecular distances are shown in Fig. 1. The crystal structure of *m*-nitroaniline hydrochloride (Fig. 2) is composed of layers of *m*-nitroanilinium ions. These layers are held together by ionic forces and hydrogen bonds. The $-NH_3^+$ group is a donor in three hydrogen bonds with chloride as acceptors. The average distance between the N atom and the Cl^- ions is 3·17 Å. Fuller (1959) found the mean value of this type of hydrogen bond to be 3·19 (7) Å [in *p*-nitroaniline hydrochloride we found it to be 3·19 Å, in *o*-nitroaniline hydrochloride 3·12 Å (Ploug-Sørensen & Andersen, 1982, 1983)]. Details of the molecular structures of *m*-nitroaniline and of the *m*-nitroanilinium ion are given in Figs. 3 and 4. The carbon rings are planar (see deposition footnote), N(2) lies in the plane defined by C(3), O(1) and O(2). In both structures the nitro group is bent out of the ring plane [dihedral angle between the ring plane and the nitro group is 3·1 (5)° in *m*-nitroaniline and 4·7 (2)° in *m*-nitroaniline hydrochloride].

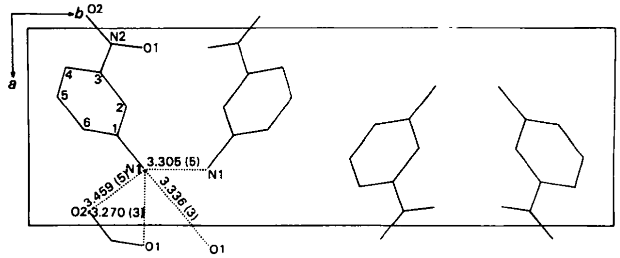

Fig. 1. The structure of *m*-nitroaniline viewed down the *c* axis. Contact distances in Å (e.s.d.'s in parentheses).

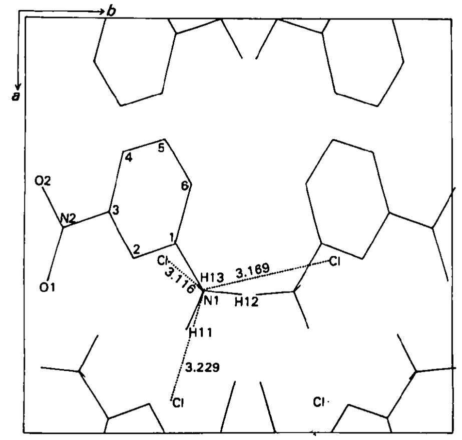

Fig. 2. The structure of *m*-nitroaniline hydrochloride viewed down the *c* axis. Contact distances in Å (e.s.d.'s are 0·001 Å).

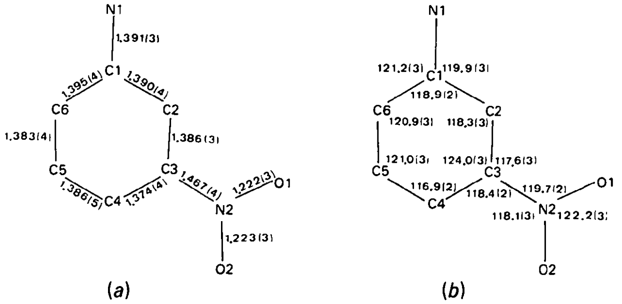

Fig. 3. (*a*) The molecular structure of *m*-nitroaniline. Bond lengths in Å. (*b*) The molecular structure of *m*-nitroaniline. Angles in degrees. (E.s.d.'s in parentheses.)

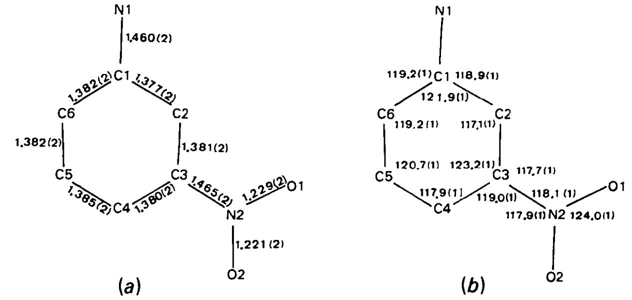

Fig. 4. (*a*) The molecular structure of *m*-nitroaniline hydrochloride. Bond lengths in Å. (*b*) The molecular structure of *m*-nitroaniline hydrochloride. Angles in degrees. (E.s.d.'s in parentheses.)

The change in structure on protonation of amines involves the bond between the nitrogen atom of the amino group and the carbon atom to which it is attached (Figs. 3*a* and 4*a*). There is a lengthening of this bond when anilines are protonated. The C(6)—C(1)—C(2) angle opens when anilines are protonated (Figs. 3*b* and 4*b*). We found the same relations for *p*-nitroaniline and *p*-chloroaniline (Ploug-Sørensen & Andersen, 1982, 1985).

Skapski & Stevenson (1973) found two very short bonds, C(1)—C(2) = 1·366 (16) and C(4)—C(5) = 1·348 (16) Å, and a very long bond, C(6)—C(1) = 1·419 (15) Å. In our determination the C—C bonds are of the same length within the limits of accuracy.

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