Table 3. ^{1}H *NMR data at* 298 K *and possible values of the torsion angle* φ

Residue	Proton	Chemical shift (p.p.m.)	Coupling constant (Hz)	δNH/dT ($\times 10^{-3}$p.p.m. K^{-1})	φ(°)
Gly	α_1	3·80	5·5 ($J_{\mathrm{NH}-\alpha}$)		±68, −128
	α_2				
	NH	5·34		6·0	
Gly	α_1	3·93	5·5 ($J_{\mathrm{NH}-\alpha_1}$)		±63, −133
	α_2	3·92	5·0 ($J_{\mathrm{NH}-\alpha_2}$)		
	NH	7·02		8·0	
Phe	α	4·82	8·0 ($J_{\mathrm{NH}-\alpha}$)		−94, −146
	β_1	3·12	6·0 ($J_{\alpha-\beta_1}$)		
	β_2	3·04	6·5 ($J_{\alpha-\beta_2}$)		
	NH	6·81		9·0	
Boc	CH_3	1·45			
Ethyl ester	CH_2	1·22			
	CH_3	4·14			

Estimated errors of chemical shift and coupling constant are ± 0·02 p.p.m. and ±0·2 Hz respectively. The values of δNH/dT were measured from the variation of the NH proton at 273, 283, 288, 293, 298 and 303 K.

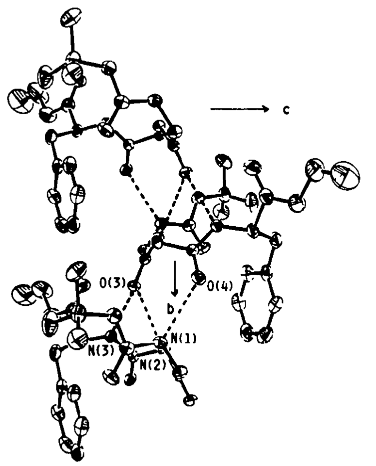

Fig. 3. The molecular arrangement of Boc-Gly-Gly-Phe-OC_2H_5 viewed along the *a* axis. The hydrogen bonds are shown by dotted lines.

The molecular arrangement projected along the *a* axis is shown in Fig. 3, in which the dotted lines represent hydrogen bonds. The folded Gly-Gly moiety of the molecule is arranged around the 2_1 screw axis parallel to the *b* axis; the molecule is linked with the neighboring molecules by three hydrogen bonds between peptide amino and carboxyl groups [N(1)···O(4) 2·822 (6), H(1)···O(4) 1·93 (6) Å, ∠N(1)–H(1)···O(4) 169 (6)°; N(2)···O(3) 2·865 (5), H(2)···O(3) 2·15 (7) Å, ∠N(2)–H(2)···O(3) 136 (6)°; N(3)···O(3) 2·916 (6), H(3)···O(3) 1·99 (6) Å, ∠N(3)–H(3)···O(3) 162 (6)°].

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Structure of *o*-Nitroaniline Hydrochloride, $C_6H_7N_2O_2^+.Cl^-$

By G. Ploug-Sørensen and E. Krogh Andersen

Department of Chemistry, The University of Odense, Campusvej 55, 5230 *Odense M, Denmark*

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Abstract. $M_r = 174·6$, orthorhombic, *Pbca*, $a = 7·878$ (2), $b = 7·940$ (2), $c = 23·73$ (1) Å, $V = 1484·3$ (8) Å^3, $Z = 8$, $D_m = 1·560$, $D_x = 1·562$ (1) Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0·46$ mm^{-1}, $T = 295$ K. Final $R = 0·07$ for 1621 observed reflexions. Layers of anilinium ions are held

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together by ionic forces and hydrogen bonds (average N–H···Cl distance is 3·12 Å). The nitro group is twisted by 26·1° with respect to the ring plane, presumably to relieve overcrowding of the nitro and amino groups.

Introduction. As a part of a programme of structure determinations of substituted anilines and substituted aniline hydrochlorides the structure of the title compound is reported. The aim of the programme is to determine the changes in molecular structure of anilines on protonation.

Experimental. Crystals were obtained by adding gaseous hydrogen chloride to a solution of *o*-nitroaniline in ether. This product was recrystallized from a mixture of ethanol and concentrated hydrochloric acid. The recrystallized product was dried in a desiccator, first over potassium hydroxide and then over phosphorus pentoxide. The formula weight was determined to 178 (theoretical value 174·59) by titration with 0·1 *M* sodium hydroxide.

Colourless prisms, 0·7 x 0·4 x 0·25 mm, Enraf–Nonius AD 3, graphite-monochromatized Mo $K\alpha$, lattice parameters from Guinier–Hägg photographs with Cu $K\alpha_1$ ($\lambda = 1{\cdot}54051$ Å) and SiO_2 as internal standard, 2128 unique reflections ($h, k, l \geq 0$) with $2{\cdot}5 < \theta < 30°$, 1621 with $I > 2{\cdot}5\,\sigma(I)$, ω scan with 2·0° interval, standard reflection 308 stable, systematic absences $0kl$ with k odd, $h0l$ with l odd and $hk0$ with h odd, Lp correction, absorption ignored; direct methods, anisotropic full-matrix least-squares refinements of non-H atoms, four fixed H included (H in NH_3^+ not locatable), $\sum w(\Delta|F|)^2$ minimized, final $R = 0{\cdot}074$ and $R_w = 0{\cdot}115$,* weights $w = 1/(12{\cdot}0 + |F_o| + 0{\cdot}06|F_o|^2)$ gave average $w\Delta(|F|)^2$ almost independent of $\sin\theta$ and $|F_o|$, scattering factors from *International Tables for X-ray Crystallography* (1962), $F(000) = 720$, computer programs from XRAY system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).

Discussion. Final atomic coordinates and equivalent isotropic temperature factors are given in Table 1.

The content of one unit cell is shown in Fig. 1. The crystal structure is composed of layers of anilinium ions. These layers are held together by ionic forces and hydrogen bonds. The H atoms at the NH_3^+ group could be located unambiguously in the difference electron density maps, but the NH_3^+ group appears to be a donor in three hydrogen bonds in which chloride ions are acceptors. The average distance between N atoms and the accepting chloride ions is 3·12 Å. Fuller (1959) found the mean value of this type of hydrogen bond to be 3·19 ± 0·07 Å.

Details of the molecular structure of *o*-nitroaniline hydrochloride are given in Table 2 and in Fig. 2(*a*) and (*b*). From Table 2 it is concluded that the aromatic ring is planar, and N(2) is out of the plane defined by C(2)O(1)O(2). The nitro group is twisted around the C(2)–N(2) bond (dihedral angle between the ring

Table 1. *Final atomic coordinates* (×10⁴) *and equivalent isotropic temperature factors* (Å²) *with e.s.d.'s in parentheses*

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

	x	y	z	B_{eq}
Cl(1)	1994 (1)	2109 (1)	7144 (1)	2·84 (4)
C(1)	1623 (5)	356 (5)	3546 (2)	1·94 (12)
C(2)	1265 (5)	−388 (5)	4068 (2)	2·14 (13)
C(3)	2549 (7)	−947 (6)	4421 (2)	2·83 (16)
C(4)	4207 (6)	−738 (6)	4256 (2)	3·00 (17)
C(5)	4579 (5)	6 (7)	3745 (2)	2·91 (17)
C(6)	3299 (5)	538 (6)	3389 (2)	2·54 (15)
N(1)	324 (4)	858 (5)	3144 (1)	2·41 (13)
N(2)	−463 (5)	−526 (5)	4274 (1)	2·80 (14)
O(1)	−1493 (4)	490 (6)	4101 (2)	3·97 (16)
O(2)	−763 (5)	−1609 (6)	4629 (2)	4·73 (19)

Table 2. *Deviations in Å of atoms from planes through the o-nitroanilinium ion*

The mean e.s.d. on the distances of C, O and N atoms from the plane is 0·005 Å.

Plane (I): C(1)–C(6)

C(1), −0·000; C(2), 0·006; C(3), −0·005; C(4), −0·001;
C(5), 0·006; C(6), −0·006; H(3), 0·175; H(4), 0·193;
H(5), 0·124; H(6), 0·106; N(1), −0·081; N(2), 0·094;
O(1), 0·622; O(2), −0·316

Plane (II): C(2), O(1), O(2)

N(2), −0·021

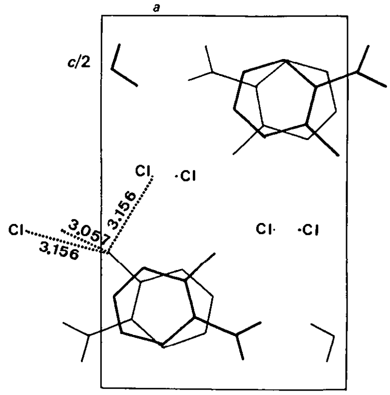

Fig. 1. The structure viewed down the *b* axis. Contact distances are in Å; e.s.d.'s are 0·004 Å.

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* Lists of structure factors, anisotropic temperature parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38164 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

plane and the nitro group 26·1°). This is probably caused by overcrowding of the nitro and amino groups. The angle N(1)—C(1)—C(2) is 5·7° larger than the angle N(1)—C(1)—C(6) and the N(1) and N(2) atoms are bent out of the ring plane in opposite directions [N(1) by −0·08, N(2) by +0·09 Å]. The C(1)—C(2) bond is significantly longer than the other five C—C bonds. The latter bonds appear to be of equal length.

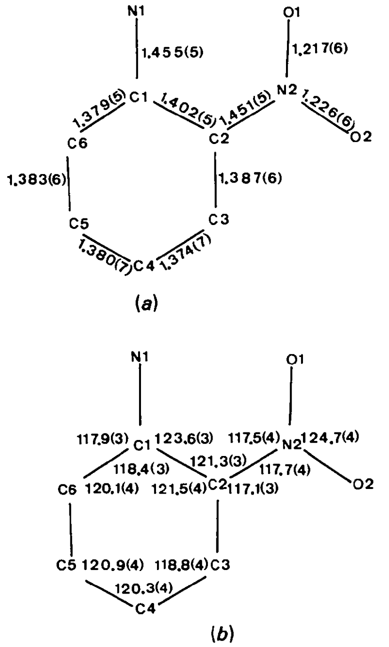

Fig. 2. The molecular structure of *o*-nitroaniline hydrochloride. (*a*) Bond lengths in Å. (*b*) Angles in degrees. (Values in parentheses are standard deviations.)

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Structures of 1-[(2*S*,3*S*)-2-(*N*,*N*-Dibenzylamino)-3-methyl-1-pentyl]pyridinium *p*-Toluenesulphonate, $C_{25}H_{31}N_2^+.C_7H_7O_3S^-$, and 1-[(2*S*)-2-(*N*,*N*-Dibenzylamino)-1-propyl]pyridinium *p*-Toluenesulphonate, $C_{22}H_{25}N_2^+.C_7H_7O_3S^-$

By Hans Razenberg, Jan A. Kanters, Jean C. Schoone and Albert J. M. Duisenberg

Structural Chemistry Group, Rijksuniversiteit Utrecht, Transitorium 3, *Padualaan* 8, 3508 *TB Utrecht, The Netherlands*

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Abstract. $C_{25}H_{31}N_2^+.C_7H_7O_3S^-$ (ILO), $M_r = 530{\cdot}74$, monoclinic, $P2_1$, $a = 11{\cdot}551$ (1), $b = 10{\cdot}428$ (1), $c = 12{\cdot}357$ (1) Å, $\beta = 94{\cdot}72$ (1)°, $V = 1483{\cdot}4$ Å^3, $Z = 2$, $F(000) = 568$, $D_x = 1{\cdot}147$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 0·146 mm^{-1}, final $R = [\sum(|F_o| - |F_c|)/\sum F_o] = 0{\cdot}042$ for 1733 unique reflections. $C_{22}H_{25}N_2^+.C_7H_7O_3S^-$ (ALO), $M_r = 488{\cdot}64$, orthorhombic, $P2_12_12_1$, $a = 15{\cdot}225$ (6), $b = 9{\cdot}663$ (5), $c = 17{\cdot}822$ (16) Å, $V = 2622$ (4) Å^3, $Z = 4$, $F(000) = 1040$, $D_x = 1{\cdot}190$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 0·158 mm^{-1}, final $R = 0{\cdot}045$ for 989 unique reflections. Both ILO and ALO are salts composed of a positively charged pyridinium moiety and a negatively charged tosyl group. With the exception of one of the phenyl rings, the structures of the pyridinium moieties of ILO and ALO are almost superimposable. The conformation about the C–C bond connecting the amino-group and pyridinium-ring N atoms is *gauche*, which results in crowded structures and short contacts between these N atoms, 2·926 (4) and 2·908 (11) Å for ILO and ALO respectively.

Introduction. Treatment of *N*,*N*-dibenzyl-L-isoleucinol with *p*-toluenesulphonyl chloride in pyridine did not result in the expected tosyl derivative, but yielded a crystalline solid of composition $C_{32}H_{38}N_2O_3S$ (within 0·1%) according to elemental analysis. Conductivity experiments and mass spectroscopy indicated the

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