

# *Ab initio* structure determination of *m*-toluidine by powder X-ray diffraction

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The powder X-ray diffraction pattern of the crystalline phase of *m*-toluidine has been recorded with a sensitive curved detector (CPS120) at 150 K. The structure has been solved by real-space methods (simulated annealing) followed by Rietveld refinements with phenyl rings as rigid bodies and with soft constraints on bond lengths for peripheral atoms. The cell is monoclinic with space group  $P2_1/c$  and  $Z = 8$ . Equivalent molecules form chains along  $c$ . The crystalline cohesion is achieved by N—H...N hydrogen bonds between neighbouring chains of non-equivalent molecules and by van der Waals interactions of neighbouring chains of equivalent molecules. The hydrogen-bonding network has been confirmed by lattice-energy minimization. Anisotropic strain effects of the cell have been calculated. The directions of the minimal strains correspond to the directions of the hydrogen bonds. An explanation of the difficulty to crystallize the metastable phase is given.

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## 1. Introduction

*m*-Toluidine (3-methylbenzenamine,  $\text{CH}_3\text{C}_6\text{H}_4\text{NH}_2$ , herein after referred to as *m*-toluidine) is a typical example of a fragile glass-forming liquid according to Angell's definition (Angell, 1991). For this reason, it has been the subject of a considerable number of experimental works (Alba-Simionesco & Krauzman, 1995; Descamps *et al.*, 1997; Morineau *et al.*, 1998; Morineau & Alba-Simionesco, 1998; Alba-Simionesco *et al.*, 1998; Dreyfus *et al.*, 1998; Aouadi *et al.*, 2000) and theoretical considerations (Morineau & Alba-Simionesco, 1998; Chelli *et al.*, 2002) in order to elucidate its structural and dynamical properties in the solid state.

*m*-Toluidine is liquid at room temperature. It can be easily supercooled, even at very low cooling rates, and gives rise to a calorimetric glass transition at  $T_g \simeq 186$  K. As the metastable liquid below  $T_g$  can be kept for several days without any sign of crystallization, *m*-toluidine is a very good example for the study of such phases. Crystallization is achieved by reheating the sample rapidly. By X-ray diffraction, Legrand *et al.* (1999) have observed two crystalline phases: a metastable phase ( $\beta$ -phase), which appears at temperatures lower than 227 K, and a stable one ( $\alpha$ -phase), with a melting temperature of 242 K.

Knowledge of the crystal structure of the subjacent stable phase is generally useful to draw some conclusions concerning the glassy phase. For example, the X-ray pattern of the glassy phase of *m*-toluidine exhibits a characteristic 'pre-peak' at low

scattering vector ( $\sin \theta/\lambda \simeq 0.080 \text{ \AA}^{-1}$ ; Descamps *et al.*, 1997). This pre-peak has been interpreted as a consequence of an intermediate-range order due to a hydrogen-bonding network. The determination of the crystal structure of its stable phase appears to be a crucial step to confirm the ability of *m*-toluidine to form hydrogen bonds. Since *m*-toluidine is a glass former, it is difficult to obtain single crystals, though the structure is very simple with eight atoms per molecule lying in a plane.

The present work is dedicated to the *ab initio* structure determination of crystalline  $\alpha$ -*m*-toluidine (the stable phase of *m*-toluidine) at 150 K from powder X-ray diffraction data. The structure determination was performed with a simulated-annealing method followed by Rietveld refinements using a rigid-body model for the phenyl groups and soft constraints on the bond lengths for bonds connecting phenyl to methyl and amine groups [see, for example, Harris & Tremayne (1996) or McCusker *et al.* (1999) for review articles on Rietveld refinements]. Energy-minimization calculations are performed in order to confirm the hydrogen-bonding network found by Rietveld refinements.

## 2. Experimental and data analysis

### 2.1. Data collection

Liquid *m*-toluidine is commercially available (Aldrich Chemical Company) with a purity rate of 99%. Contacts with air or light easily induce oxidation which gives rise to a typical brown-coloured compound. Further purifications are neces-

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sary, consisting of two stages of removal of organic and inorganic impurities. The compound is then distilled under low pressure, in order to obtain a colourless compound.

The powder X-ray diffraction patterns were recorded using the laboratory diffractometer equipped with an INEL sensitive curved detector, CPS120. A bent quartz monochromator enables the selection of the  $K\alpha_1$  wavelength of a Cu X-ray tube ( $\lambda = 1.54056 \text{ \AA}$ ). The liquid sample, introduced in a Lindemann glass capillary (diameter = 0.7 mm) was mounted on the axis of the diffractometer. It was rotated during the experiment in order to reduce the effect of possible preferential orientation. The calibration of the curved detector was performed with the X-ray diffraction pattern of the standard compound  $\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$  (NAC; Evain *et al.*, 1993). A cubic spline interpolation was performed between the peaks of NAC. As the first peak of NAC appears at  $2\theta = 12.2^\circ$ , the calibration for angles lower than this value is not very good and for the refinements, this part of the pattern is discarded. This pattern of NAC is also used to determine the parameters of the Caglioti function (Caglioti *et al.*, 1958) for the experimental resolution. Their values are:  $U_{\text{ins}} = 0.0085$ ,  $V_{\text{ins}} = -0.0033$  and  $W_{\text{ins}} = 0.0065 (\text{^\circ})^2$ .

A cold-nitrogen blower (Cryostream Oxford Cryosystem) enabled access to low temperatures with temperature fluctuations within 0.5 K, and was used for the *in situ* crystallization according to the following procedure. The liquid *m*-toluidine was quenched at 130 K by directing the cold stream on the capillary. After the temperature stabilization, the sample was heated to 220 K at a rate of  $6 \text{ K min}^{-1}$ . It was kept at this temperature for about 15 h in order to achieve complete crystallization of the powder. Finally, the sample was cooled to the experiment temperature. Data were collected at 150 K with a total counting time of about 24 h. In order to

perform neutron diffraction measurements, the fully deuterated compound was synthesized. However, attempts to obtain crystallized powder with the thermal processing described above always failed.

## 2.2. Structure solution and refinement

To determine the lattice parameters of *m*-toluidine at 150 K, the automatic powder indexing program *N-TREOR* (Altomare *et al.*, 2000) implemented in *EXPO* (Altomare *et al.*, 1999) was used initially. With the first 25 reflections of the pattern, no solution was found, raising the possibility of several phases in the powder. With the program *WinPlotr* (Roisnel & Rodriguez-Carvajal, 2002), the profiles of the 38 reflections with  $2\theta$  angles lower than  $36^\circ$  were individually refined with a pseudo-Voigt function in order to obtain their  $2\theta$  positions. The  $2\theta$  angles of the 15 more intense reflections were introduced in the program *TREOR* (Werner *et al.*, 1985) and these lines were completely indexed with a monoclinic cell with the following parameters:  $a = 24.815$ ,  $b = 5.799$ ,  $c = 8.743 \text{ \AA}$ ,  $\beta = 100.03^\circ$ ,  $V = 1238.8 \text{ \AA}^3$ . The calculated figures of merit are:  $M(15) = 31$ ,  $F(15) = 43$  (0.038, 94) (de Wolff, 1968; Smith & Snyder, 1979). It is notable that the relation between the lattice parameters  $2a \cos \beta + c = 0$  is nearly verified, leading to a pseudo-*B*-faced orthorhombic cell. As a consequence, the two reflections in the monoclinic cell,  $(h, k, l)$  and  $(-h - l, k, l)$ , with  $h$  and  $l > 0$ , have approximately the same *d*-spacing.

The powder diffraction pattern from 12 to  $72^\circ 2\theta$  was subsequently refined with this cell and with resolution constraints in the monoclinic space group *P2/m* (a space group without systematic extinctions) using the 'profile matching' option [Le Bail *et al.* (1988) profile refinement] of the program *FullProf* (Rodriguez-Carvajal, 2001). Five lines with low intensity were not indexed with the previous cell and may correspond to a second phase due to an impurity (Fig. 1). With the program *TREOR*, it is possible to find a monoclinic cell with these five reflections, but it seems more realistic to remove regions of the pattern corresponding to these reflections (about  $\pm 0.20^\circ 2\theta$  around the maximum of the peaks) to avoid the introduction of this cell in the refinements. A possible chemical impurity is *m*-nitrotoluene resulting from the oxidation of the amine group of *m*-toluidine.

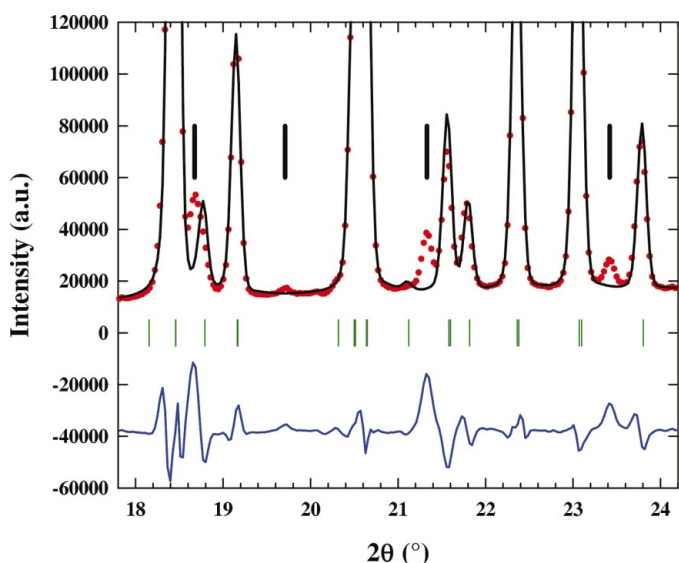
The profile of the reflections is a pseudo-Voigt function with the same full width at half-maximum (FWHM) values for the Gaussian and the Lorentzian components. This FWHM has a  $\theta$  dependence according to the Caglioti law (Caglioti *et al.*, 1958). The Lorentzian and Gaussian contributions in the pseudo-Voigt function are given by the relation

$$\text{pV}(x) = \eta L(x) + (1 - \eta)G(x),$$

where the parameter  $\eta$  has a linear dependence on  $\theta$ :

$$\eta = \eta_0 + X(2\theta).$$

The background is determined with a linear interpolation between 30 points regularly distributed from 12 to  $72^\circ 2\theta$ . For these Le Bail refinements, there are 42 parameters: four lattice parameters; the zero-point parameter; five parameters for the profile function ( $U$ ,  $V$  and  $W$  of the Caglioti function,  $\eta_0$  and



**Figure 1**

The four most intense Bragg reflections due to an impurity. Dots correspond to observed data, the upper solid line is the calculated profile for *m*-toluidine and the lower line is the difference between the observed and calculated patterns. The fine vertical bars indicate the positions of Bragg peaks for *m*-toluidine, while the thick bars are for the impurity.

$X$ ); two parameters for the asymmetry of the peak according to the Bérar & Baldinozzi (1993) function; 30 points for the background.

Systematic absences of  $(0, k, 0)$  reflections with  $k$  odd and  $(h, 0, l)$  reflections with  $l$  odd lead to the space group  $P2_1/c$ . The profile reliability factors obtained after the Le Bail refinements are  $R_p = 0.0594$ ,  $R_{wp} = 0.0720$ ,  $R_{exp} = 0.0115$  and  $\chi^2 = 39.3$ . The lattice parameters are:  $a = 24.8677$  (11),  $b = 5.8046$  (3),  $c = 8.7555$  (5) Å,  $\beta = 100.199$  (2)°,  $V = 1243.9$  (1) Å<sup>3</sup>.

The density of the solid phase of *m*-toluidine is not known, but for the liquid phase at room temperature, the measured density is  $0.989 \text{ g cm}^{-3}$  (Handbook of Chemistry and Physics, 1997–1998). With the cell volume at 150 K obtained above, and eight molecules per unit cell, the calculated density is equal to  $1.142 \text{ g cm}^{-3}$ , which is consistent with the value for the liquid phase; it can be concluded that the number of molecules in the asymmetric unit is  $Z' = 2$ . This number of molecules per unit cell is also in agreement with the Kempster & Lipson (1972) 'rule of thumb', namely  $18 \text{ Å}^3$  per non-H atom.

To obtain a starting structural model and despite the presence of a second phase due to an impurity, the 'parallel tempering' algorithm of the program *FOX* (Favre-Nicolin & Cerny, 2002) was used. Two molecules of *m*-toluidine, without the H atoms, were introduced randomly in the monoclinic cell calculated by the Le Bail refinements. The phenyl group of the molecule was taken as a regular hexagon with an edge of  $1.395 \text{ Å}$ ; the C atom of the methyl group and the N atom were located geometrically with C—C and C—N bond lengths of  $1.52$  and  $1.38 \text{ Å}$ , respectively. The intensities calculated with *FOX* in direct space were compared with the experimental X-ray pattern at  $150 \text{ K}$  and in the  $2\theta$  range from  $12$  to  $60^\circ$ . After about 10 million trials, the reliability factor  $R_{wp}$  fell to  $0.175$ .

Atomic coordinates found by *FOX* were introduced in the program *DEBVIN* (Brückner & Immirzi, 1997), which enables the refinement, with a least-square procedure, of the generalized coordinates, and allows H atoms to be input. The two phenyl groups were always considered as rigid. The C atom of the methyl group and the N atom could move by means of their bond angles and their torsion angles C—C—C—C and C—C—C—N, respectively. The four H atoms of the phenyl groups were located with geometrical arguments. The three H atoms of the methyl group were located symmetrically around the C—C bond and were able to rotate around this axis. The two H atoms of the amine group were placed such that the C—NH<sub>2</sub> atoms lay in the same plane and this plane could rotate around the C—N bond. The two molecules could translate and rotate around their mass centre. A global temperature factor was fitted for each molecule. The second phase was neglected in the program *DEBVIN*. The program employed 57 variable parameters: nine profile parameters (four lattice parameters, the zero-point,  $U$ ,  $V$ ,  $W$  of the Caglioti function, and  $\eta_0$  which mixes Gaussian–Lorentzian profiles); 28 structural variables (the scale factor, a parameter to take into account preferred orientations found along  $[001]$ , and, for each of the two

molecules, three degrees of translation and three degrees of rotation of the whole molecule, two bond angles, four torsion angles and a global isotropic temperature factor); 20 background points.

For a  $2\theta$  range from  $12$  to  $72^\circ$ , the  $R_{wp}$  index ( $R'_3$  in *DEBVIN*) was  $13.6\%$ . As C and N atoms have almost the same X-ray atomic scattering factors and in the solution given by *FOX* the C of the methyl group and the N can be inverted, trials were run by interchanging these two atoms in *DEBVIN*. The  $R_{wp}$  indices for these refinements were less good and the positions of these two atoms were kept as in *FOX*.

The advantage with the use of *DEBVIN* lies in the possibility to fit generalized coordinates of non-H atoms when geometrical constraints are maintained for H atoms during the refinements. In fact, *DEBVIN* produces few choices for the Bragg peak shape functions.

Subsequently, the atomic coordinates found by *DEBVIN* were introduced in *FullProf* in order to perform Rietveld refinements.

To limit the number of adjustable parameters in *FullProf*, the two phenyl groups were kept planar and rigid, with C—C and C—H bond lengths equal to  $1.395$  and  $0.98 \text{ Å}$ , respectively, and bond angles equal to  $120^\circ$ . The coordinates of the two last non-H atoms of the molecule (N and C of the methyl groups) were refined with soft constraints on their bond lengths. The required C—C and C—N bond lengths were  $1.52$  and  $1.38 \text{ Å}$ , respectively, with a standard deviation of  $0.01 \text{ Å}$ . The starting coordinates of the H atoms of the methyl and amine groups were those found with *DEBVIN* and, in a first step, their positions were not refined. Each molecule had a global isotropic temperature factor. Intensities were corrected with respect to the absorption effects for a cylindrical sample with a  $\mu R$  value of  $0.18$ .

For the peak-shape function, a Thompson–Cox–Hastings profile function (Thompson *et al.*, 1987) was used, taking into account experimental resolution, strain and size effects. The FWHM of the Gaussian ( $H_G$ ) and Lorentzian ( $H_L$ ) components of the peak profile have an angular dependence given by (Rodriguez-Carvajal, 2001)

$$H_G^2 = [(U_D + U_{ins}) + (1 - \zeta)^2 D_{ST}^2(\alpha_D)] \tan^2 \theta + V_{ins} \tan \theta + W_{ins} + I_G / \cos^2 \theta$$

and

$$H_L = [X + \zeta D_{ST}(\alpha_D)] \tan \theta + [Y + F(\alpha_Z)] / \cos \theta.$$

In these relations,  $U_{ins}$ ,  $V_{ins}$  and  $W_{ins}$  are the parameters of the Caglioti function for the experimental resolution, determined with the NAC pattern; they are not refined in the following.  $U_D$ ,  $D_{ST}(\alpha_D)$  and  $X$  have a meaning in terms of strain and  $I_G$ ,  $Y$  and  $F(\alpha_Z)$ , in terms of size. Each one of the two contributions can be isotropic, with  $U_D$ ,  $X$  and  $Y$ , or anisotropic, with  $D_{ST}(\alpha_D)$  and  $F(\alpha_Z)$ . The parameter  $\zeta$  is a mixing coefficient to mimic the Lorentzian contribution to strains.

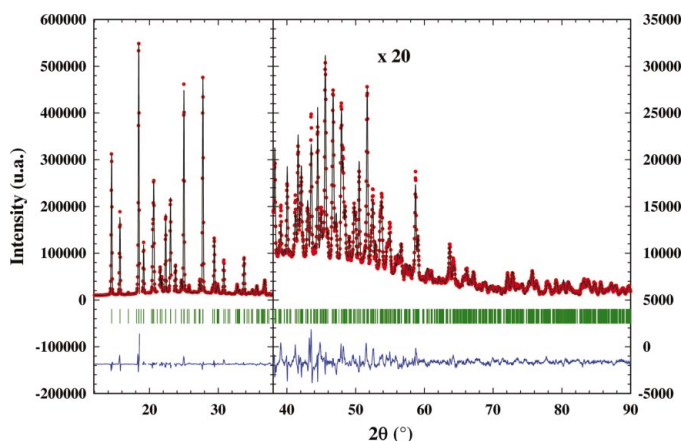
For the preferred orientations, with the March (1932) and Dollase (1986) function, the direction yielding the better agreement factors is  $[001]$ . To determine from the shape of the

**Table 1**

Crystallographic data for  $\alpha$ -*m*-toluidine at 150 K obtained after Rietveld refinements.

Formula	C <sub>7</sub> H <sub>9</sub> N
$M_r$	107.15
Crystal system	Monoclinic
Space group	$P2_1/c$
$a$ (Å)	24.8727 (6)
$b$ (Å)	5.8073 (2)
$c$ (Å)	8.7615 (3)
$\beta$ (°)	100.062 (2)
$V$ (Å <sup>3</sup> )	1246.07 (6)
$Z$	8
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	1.142
$F(000)$	464
$\mu$ (mm <sup>-1</sup> )	0.52
$2\theta$ range (°)	12–90
Step size (° $2\theta$ )	0.029
Wavelength (Å)	1.54056
No. of profile data steps	2690
No. of contributing reflections	999
No. of structural variables	40
No. of profile parameters	18
No. of background points refined	34
No. of bond length constraints	8
$R_p$	0.0750
$R_{wp}$	0.0855
$R_{exp}$	0.0129
$\chi^2$	43.8
$R_B$	0.0404
$R_F$	0.0492

peaks if the size and strain effects are isotropic or anisotropic, several trials were made for a  $2\theta$  range from 12 to 90° and excluding the four regions where the second phase appears. When the two effects are taken as isotropic, the agreement factors are  $R_p = 0.0908$ ,  $R_{wp} = 0.0999$ ,  $\chi^2 = 58.8$ ; with isotropic size effects and anisotropic strain effects using the Stephens (1999) formulation for  $D_{ST}(\alpha_D)$ , the indices become  $R_p = 0.0751$ ,  $R_{wp} = 0.0874$ ,  $\chi^2 = 45.4$ . Finally, with the two anisotropic effects and a development in spherical harmonics for  $F(\alpha_Z)$  (Popa, 2000),  $R_p = 0.0718$ ,  $R_{wp} = 0.0830$ ,  $\chi^2 = 41.1$ ; the improvement of the agreement factors is not very important

**Figure 2**

Final Rietveld plot of *m*-toluidine at 150 K. Observed data points are indicated by dots, the best-fit profile (upper trace) and the difference pattern (lower trace) are solid lines. The vertical bars correspond to the positions of Bragg peaks.

with respect to the previous case and, for some directions, the value of the strain becomes negative. For these reasons, in the following, the size effects will be taken as isotropic and the strain effects as anisotropic.  $X$  and  $\zeta$  are found to be equal to 0, such as when the strain effects have Gaussian components only.

From preliminary calculations of intermolecular contacts, the shortest distances between N atoms are found to be 3.311 Å, between N1 and N2 of the asymmetric unit, and 3.166 Å, between N2 and N1( $x, -y - 1/2, z + 1/2$ ), leading to the possibility of hydrogen bonds of the type N—H...N. Thus, the existence of hydrogen bonds is exclusively determined by the relative positions of the H atoms of the amine groups with respect to the N atoms. According to the hydrogen-bonding scheme, molecules can form either dimers or chains. As it was impossible to crystallize deuterated *m*-toluidine in order to perform neutron diffraction experiments, the methods used in this paper to locate these H atoms are Fourier syntheses and lattice-energy minimization.

The four H atoms of the amine groups were removed from the previous Rietveld refinements, and new refinements were performed. Surprisingly, the values of the agreement factors became  $R_p = 0.112$ ,  $R_{wp} = 0.124$  and  $\chi^2 = 91.8$  ( $R_{wp}$  increased by about 3.7% after the removal of only four electrons among the 116 electrons in the asymmetric unit). Fourier syntheses calculated with *SHELX97* (Sheldrick, 1997) show four peaks of electron density between 0.23 and 0.38 e Å<sup>-3</sup> in the vicinity of the N atoms. The coordinates of these peaks were introduced as H atoms of the amine groups in the Rietveld calculations. Taking into account the large difference in  $R_{wp}$  when H atoms are removed, the coordinates found by Fourier syntheses were fitted with soft constraints of 1.01 Å on N—H bond lengths. For the other atoms and for the peak-shape function, refinements were performed with the same parameters as above. Finally, for a  $2\theta$  range from 12 to 90° with four regions excluded to avoid the second phase, there were 92 adjustable parameters: 18 profile parameters [the zero-point parameter, four lattice parameters,  $Y$ ,  $I_G$ , nine parameters for the anisotropic strain effects and two parameters of the Bérar & Baldinozzi (1993) function for the asymmetry of the peaks]; 40 structural variables [the scale factor, a parameter ( $G_1$ ) linked to preferred orientations according to the March (1932) and Dollase (1986) function, and, for each molecule, three degrees of translation and three degrees of rotation of the whole molecule, the three coordinates of  $Ci7$ ,  $Ni$ ,  $HNi1$  and  $HNi2$ , and a global isotropic temperature factor (there were also eight soft constraints on bond length for the previous atoms)]; 34 background points.

The final Rietveld agreement factors are  $R_p = 0.0750$ ,  $R_{wp} = 0.0855$ ,  $R_{exp} = 0.0130$  and  $\chi^2 = 43.8$ . Note the small value of  $R_{exp}$  due to large counting values; as a consequence,  $\chi^2$  is high. Another reason for the high  $\chi^2$  values obtained with a curved detector could be residual small errors in the  $2\theta$  values as a result of the use of a calibration procedure. The plot of the X-ray pattern is given Fig. 2 and crystallographic data are presented in Table 1. Profile parameters,  $G_1$  and isotropic temperature factors are reported Table 2. The molecular

**Table 2**

Profile and some structural parameters for  $\alpha$ -*m*-toluidine at 150 K obtained with the program *FullProf* after Rietveld refinements.

$Y$	0.0187 (6)
$I_G$	0.0008 (1)
$S_{400}$	0.0044 (2)
$S_{040}$	0.697 (40)
$S_{004}$	0.183 (8)
$S_{220}$	0.082 (8)
$S_{202}$	−0.025 (4)
$S_{022}$	0.372 (39)
$S_{121}$	0.134 (37)
$S_{301}$	0.013 (2)
$S_{103}$	−0.060 (8)
$Asym_1$	0.083 (10)
$Asym_2$	0.021 (1)
Preferred orientation	[001]
$G_1$	0.914 (3)
$B_{iso}$ (Å <sup>2</sup> ), molecule 1	2.05 (16)
$B_{iso}$ (Å <sup>2</sup> ), molecule 2	2.70 (18)

**Table 3**

Hydrogen-bonding geometry (Å, °) for  $\alpha$ -*m*-toluidine at 150 K.

$D-H\cdots A$		$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—HN11 $\cdots$ N2	(a)	1.007 (83)	2.305 (84)	3.302 (15)	170 (6)
	(b)	1.005	2.456	3.295	140.6
	(c)	1.021	2.370	3.397	150.5
N2—HN22 $\cdots$ N1 <sup>i</sup>	(a)	1.007 (34)	2.712 (34)	3.176 (13)	108 (3)
	(b)	1.003	2.357	3.215	143.0
	(c)	1.024	2.178	3.090	147.4

Symmetry code: (i)  $x, -y - 1/2, z + 1/2$ . Notes: (a) obtained by the X-ray experiment; (b) calculated with *PMC* (Dzyabchenko, 2001); (c) calculated with *CASTEP* (Segall *et al.*, 2002).

structure, drawn with *ORTEP3* (Farrugia, 1997), and the atomic labelling scheme are shown in Fig. 3.<sup>1</sup>

### 2.3. Lattice-energy minimization

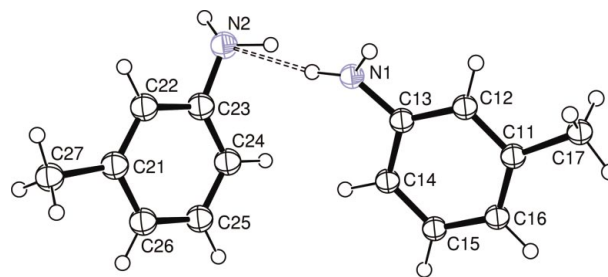
With the Rietveld refinements, the N1—HN11 $\cdots$ N2 hydrogen bond was defined unambiguously. However, two possibilities arose for the acceptor atom for the hydrogen bond starting from N2—HN22: either N1 of the asymmetric unit or N1( $x, -y - 1/2, x + 1/2$ ). Energy-minimization calculations can help to solve this problem and two different programs were used: *PMC* (Dzyabchenko, 2001) and *CASTEP* (Segall *et al.*, 2002).

With the *PMC* program (Dzyabchenko, 2001), the lattice energy comprising both the intermolecular crystal packing energy and the conformational energy was calculated with the atom–atom potentials of the 6–12 Lennard–Jones form with parameters from Momany *et al.* (1974), to account for the van der Waals energy, and the atomic charges calculated for the isolated molecule by the Gasteiger method (Gasteiger & Marsili, 1980) for the electrostatic energy. In addition to the non-bonded atom–atom potentials, the positions of the amine H atoms were governed by the link (bond-variation) poten-

tials of quadratic form  $V_{\text{link}} = w(r - r_0)^2$ , to define the equilibrium geometry of the amine group, and a torsional potential of the form  $V_{\text{tors}} = V_0 \cos^2 \tau$  to describe the  $\pi$ -electron stabilization effect due to interaction of the lone pair of electrons on the N atom with the aromatic ring. The empirical parameters  $w$ ,  $r_0$  and  $V_0$  of the link and torsional potentials of the amine group were calibrated by trial energy minimizations of the aniline crystal structure, the full crystal structure of which, including the H-atom positions, is known from a single-crystal X-ray diffraction study (Fukuyo *et al.*, 1982). Note that the role of the torsional potential was recognized in the present study as essential: without this potential, the conformation of the NH<sub>2</sub> group was predicted incorrectly.

In the final energy calculation of the *m*-toluidine structure, the lattice parameters and coordinates of atoms obtained with *Fullprof* were kept, except the coordinates of the H atoms of the amine groups. This energy minimization confirms the N1—HN11 $\cdots$ N2 hydrogen bond found by *Fullprof*, but it finds N2—HN22 $\cdots$ N1( $x, -y - 1/2, x + 1/2$ ) as the second hydrogen bond (see Table 3). Introducing these coordinates in *Fullprof* and fitting only the profile parameters, the agreement factors are  $R_p = 0.0873$ ,  $R_{wp} = 0.0991$ ,  $\chi^2 = 57.7$ , close to the values of the final Rietveld refinement.

The second lattice-energy minimization was performed with *CASTEP* (Segall *et al.*, 2002), which is an *ab initio* quantum mechanical program employing density functional theory. The lattice parameters were fixed at the values obtained with *Fullprof*; the coordinates of atoms were found by energy minimization using first principles. The average deviation between the heavy-atom positions in the optimized and refined structures is 0.11 Å for molecule 1 and 0.12 Å for molecule 2. The orientation of the N1 amine group corresponds to the refined one; thus the existence of the N1—HN11 $\cdots$ N2 hydrogen bond is confirmed. The second amine group is rotated by about 35° with respect to the orientation found by *Fullprof*, leading to a much more reasonable geometry for the N2—HN22 $\cdots$ N1( $x, -y - 1/2, x + 1/2$ ) hydrogen bond (see Table 3). The optimized coordinates were input in *Fullprof* and only the profile parameters were fitted; the agreement factors are  $R_p = 0.120$ ,  $R_{wp} = 0.136$ ,  $\chi^2 = 103$ . This is an excellent result because no atomic coordinates were adjusted in this refinement.

**Figure 3**

Atomic numbering and molecular structure of *m*-toluidine at 150 K. The dashed bond represents the hydrogen bond between the two molecules of the asymmetric unit.

<sup>1</sup> Supplementary data for this paper are available from the IUCr electronic archives (Reference: PD5008). Services for accessing these data are described at the back of the journal.



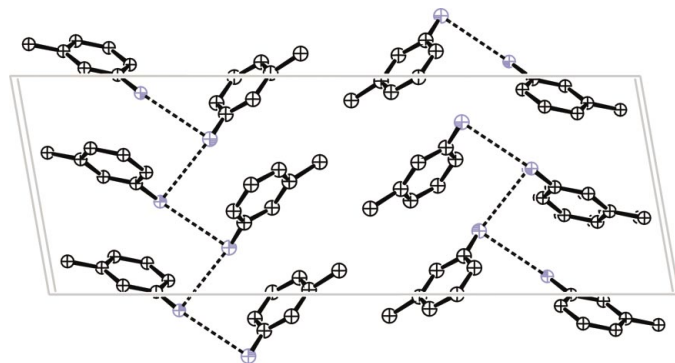
**Table 4**Equations of phenyl planes in  $\alpha$ -*m*-toluidine at 150 K.Equation for planes:  $Ax + By + Cz = D$ , where  $x$ ,  $y$ ,  $z$  and  $D$  are in Å.

Distance from phenyl plane			Constant	
Molecule 1	C17	0.110	<i>A</i>	−0.2985
	N1	−0.064	<i>B</i>	−0.4012
			<i>C</i>	−0.8660
			<i>D</i>	−9.262
Molecule 2	C27	0.017	<i>A</i>	0.6130
	N2	0.065	<i>B</i>	−0.4331
			<i>C</i>	−0.6607
			<i>D</i>	6.002

### 3. Discussion

For bond lengths, the most important difference between the Rietveld values and those obtained using the soft constraints concerns the C23–N2 bond, with a difference of 0.040 Å. Also of note are the bond angles with C17 and N1, which differ significantly from the value of 120°. From the calculated torsion angles involving HN*ij* as the terminal atom, it can be concluded that the C–NH<sub>2</sub> group is almost planar in the first molecule, the angle between the two planes C13–N1–HN11 and C13–N1–HN12 being 8 (11)°. On the other hand, for the second molecule, these four atoms are not planar: the value of the angle between the two planes C23–N2–HN21 and C23–N2–HN22 is 36 (10)°. Table 4 gives the equations of the phenyl planes with the distances of peripheral atoms from these planes. C17 and the two N atoms deviate significantly from these planes. The dihedral angle between the two phenyl planes of the asymmetric unit is 124.3 (2)°.

The crystal structure is illustrated in Fig. 4. It consists of chains along [001]. In a chain, there are, successively, a molecule and its equivalent generated by the *c*-glide plane at  $y = 1/4$ . Along [100], there are two chains of one of the two molecules of the asymmetric unit, then two chains of the second molecule. The two chains of the first molecule are located on either side of the origin of the unit cell and are related by the inversion centre. The chains formed with the second molecule exhibit the same behaviour, but two neighbouring chains are related by the inversion centre located at the middle of lattice parameter *a*.

**Figure 4**

Projection of the unit cell of *m*-toluidine along *b*. For the sake of clarity, H atoms have been omitted. Dashed lines correspond to hydrogen bonds.

For two neighbouring chains of non-equivalent molecules, the molecular interactions involve N–H...N hydrogen bonds (see Table 3 for the characteristics of these hydrogen bonds). Both Rietveld refinements and energy-minimization calculations show the existence of N1–HN11...N2 and N2–HN22...N1( $x, -y - 1/2, z + 1/2$ ) hydrogen bonds. Each N atom is both donor and acceptor, with the sequence N1–HN11...N2–HN22...N1–HN11...N2 between two adjacent chains. For the first two chains of the unit cell, this sequence runs in the opposite direction of *c*, while for the last two chains obtained from the first two by an inversion centre, it runs in the direction of *c*. The N...N bond lengths (3.176 and 3.302 Å) correspond to a slightly high value for such hydrogen bonds, the average value for which is 3.10 Å (see, for example, Glidewell *et al.*, 2003). The coordinates *y* of the N atoms of molecules of two adjacent chains are almost the same; consequently, the hydrogen bonds are approximately parallel to the (*ac*) plane. Except for these hydrogen bonds, there are few contacts between atoms of the two molecules of the asymmetric unit; those that exist concern N atoms: N1 with C23 and C24 (3.62 and 3.79 Å, respectively).

Between two chains of equivalent molecules, the cohesion is governed by intermolecular van der Waals interactions between atoms of the methyl groups. The shortest contact distances are 3.55 Å between C27 and C27( $1 - x, -y, 1 - z$ ) and 3.71 Å between C17 and C17( $2 - x, -y, 1 - z$ ). For neighbouring molecules of the same chain, there are van der Waals contacts between the N atom and the six C atoms of the phenyl group: for the first molecule, the N1...C1*i* distances range from 3.55 to 3.64 Å, while for the second one, the N2...C2*i* distances range from 3.70 to 3.80 Å. The shortest distances between two C atoms of neighbouring molecules of the same chain are 3.79 Å between C11 and C12( $x, -y - 1/2, z - 1/2$ ) and 3.68 Å between C25 and both C23( $x, -y + 1/2, z - 1/2$ ) and C24( $x, -y + 1/2, z - 1/2$ ). Along *b*, the shortest intermolecular distances are 3.52 Å between C15 and C12( $x, y + 1, z$ ) and 3.51 Å between C25 and C22( $x, y + 1, z$ ). As two successive molecules along *b* are not face-to-face, these interactions are not  $\pi$ – $\pi$  stacking interactions, but only van der Waals contacts which are stronger than along *c*. Also of note is the similarity between the structures of *m*-toluidine and aniline (C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>; Fukuyo *et al.*, 1982): they have almost the same monoclinic unit cell with eight molecules, and the intermolecular cohesion energy is achieved by hydrogen-bonds networks.

In the Rietveld refinements, a direction of preferred orientation is determined and this effect is taken into account in the Bragg peak intensity with the March (1932) and Dollase (1986) function. Best fits of the Rietveld refinements are obtained when the preferred orientation is along [001]. The parameter  $G_2$ , representing the non-textured fraction of sample, is taken as zero. The second parameter  $G_1$  is equal to 0.914, corresponding to a small needle-like habit for the crystallites.

An original aspect of Rietveld refinements of powder diffraction patterns is the possibility to determine the size and strain effects from the profile of the Bragg peaks. The size

**Table 5**

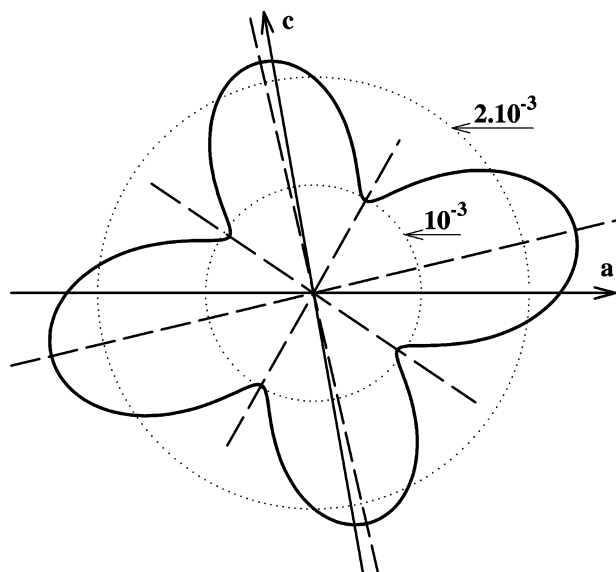
Values of the anisotropic strain ( $\Delta d/d$ ) for  $\alpha$ -*m*-toluidine at 150 K in some selected directions.

$\varphi$  is the angle between the direction  $a$  and the direction of the extreme values.

	$\varphi$	$\Delta d/d$
Minimum values in the ( $ac$ ) plane	60.5	$9.8 \times 10^{-4}$
	146.0	$9.4 \times 10^{-4}$
Maximum values in the ( $ac$ ) plane	13.5	$24.9 \times 10^{-4}$
	103.0	$21.9 \times 10^{-4}$
Value in the $b$ direction	–	$17.6 \times 10^{-4}$

effects are taken as isotropic and the calculated averaged value of the diameter of the crystallites is 1740 (10) Å. This isotropy is consistent with the conclusion made for the preferred orientation, where the crystallites have only a small needle-like habit, in fact close to a spherical shape.

On the contrary, the agreement factors are improved when the strain effects are considered as anisotropic. Fig. 5 shows values of the strain for different directions in the monoclinic plane ( $ac$ ). Table 5 reports directions and values of the calculated minimum and maximum strains in this plane and also the value along the lattice parameter  $b$ . These extreme values in the monoclinic plane constitute also the extreme values of the strain for all directions. The angles of the spherical coordinates of the hydrogen bonds are: for N1–HN11...N2,  $\theta = 85.2$  and  $94.8^\circ$ ,  $\varphi = 146.3^\circ$ , and for N2–HN22...N1( $x, -y - 1/2, z + 1/2$ ),  $\theta = 89.0$  and  $91.0^\circ$ ,  $\varphi = 51.6^\circ$ . Hydrogen bonds are almost in the ( $ac$ ) plane and the angular values of the hydrogen bonds which are the stronger intermolecular interactions of the crystal of *m*-toluidine are approximately the same as the directions of the minimum values of the strain. In the same way, the directions of the maximum values of the strain correspond to directions where the intermolecular contacts are very weak. Along  $b$ , there is an intermediate situation where the intermolecular interactions

**Figure 5**

Calculated strain in the monoclinic plane of *m*-toluidine at 150 K.

and the strain have intermediate values. Thus, for a given direction, the value of the strain of the cell of *m*-toluidine seems to be inversely proportional to the intensity of the intermolecular interaction.

#### 4. Concluding remarks

Once melted, *m*-toluidine is, upon undercooling, an excellent glass former. The compound can remain in the metastable liquid state (between the glass transition temperature  $T_g$  and the melting temperature  $T_m$ ) for an extremely long time, without any trace of recrystallization. In order to promote nucleation, then growth of crystal, it has been shown that a very specific heat treatment inducing crack formation below  $T_g$  is a necessary step to start nucleation (Legrand *et al.*, 1999).

The X-ray static structure factor of liquid *m*-toluidine,  $S(Q)$ , shows a well characterized pre-peak at  $\sin\theta/\lambda \simeq 0.080 \text{ \AA}^{-1}$  (Descamps *et al.*, 1997). Significantly before the main peak, the intensity of this pre-peak has been observed to increase when the temperature is decreased. The intermediate-range order that is thus revealed has been attributed to some distribution function of above-molecular globules. This feature has been analysed further with Monte Carlo simulations (Morineau & Alba-Simionesco, 1998). The present study suggests that the external part of the globules is formed by the phenyl rings of the molecules with hydrogen bonds pointing internally. This description of the hydrogen-bond organization in the liquid state compared with that which develops in the crystal (Fig. 4) helps to understand the difficulty in forming a critical crystalline nucleus.

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