Experimental evidence for the amino-group non-planarity in nitroanilines: neutron diffraction study of 2-methyl-5-nitroaniline at 100 K

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Abstract

An appreciable degree of pyramidalization of the amine N atom is observed in the title compound. The existence of polar chains, induced by N—H···O synthons, is confirmed. C—H···O interactions, not noted in a previous X-ray study, were found to stabilize further the known head-to-tail assembling of the chains. The structure can be described as non-polar (101) layers, embodying chains interlinked by centrosymmetric dimers, connected by C(aryl)—H···π interactions. The latter are not present in *m*-nitroaniline, 2-methyl-4-nitroaniline and other related compounds with chains built from similar N—H···O synthons and assembled head-to-head. This finding implies that an obvious relationship between molecular recognition patterns and crystal structures should not be assumed.

1. Introduction

Much effort has been devoted in the last decade to the study, design and understanding of the aggregation of organic molecules (Turi & Dannenberg, 1993, 1995, 1996; Desiraju, 1996; Aakeröy, 1997). The considerable interest in the field has been based on the fact that crystal engineering, the ability to predict and/or direct the three-dimensional arrangement, can be used to tailor materials of biological or technological importance (Desiraju, 1989). Nitroanilines have received special attention owing to their recognized second-harmonic generation capability. In particular, since the pioneering work by Etter's group (Panunto *et al.*, 1987; Etter *et al.*, 1990), which assumed that weak and bifurcated N—H···O-nitro hydrogen bonds induce polar-chain generation in nitroanilines, several semi-empirical and *ab initio* calculations on aniline-derivative aggregates have been performed (Dannenberg, 1991; Turi & Dannenberg, 1996; Hamada, 1996). These calculations have been seeking not only to rationalize the observations of Etter's group, and thus find a way of inducing

the non-centric assembling necessary for second-harmonic generation, but also to examine the validity of the oriented-gas formalism (Chemla *et al.*, 1975; Zyss & Oudar, 1982). The latter has been widely used to obtain macroscopic susceptibilities from molecular hyperpolarizabilities assuming the additivity of the molecular response. Despite the great amount of work dedicated to these topics, the interplay between intramolecular charge transfer, supramolecular assembly and non-linear optical phenomena in nitroaniline crystals has not been successfully described (Krishnamohan Sharma & Desiraju, 1994; Sarma *et al.*, 1995; Hamada, 1996). This failure has been partially ascribed to the omission of the non-planarity of the amino group (Bludsky *et al.*, 1996).

Most of the calculations involving the amino group, even those related to amino groups in nucleic acid bases, disregard its non-planarity (Bludsky *et al.*, 1996). This has probably been because of the lack of reliable experimental diffraction and gas-phase spectroscopic data. Aniline planarity has been backed by most organic text-book assumptions [see, for example, Morrison & Boyd (1987) and Fessenden & Fessenden (1990)] and even by surveys (Allen *et al.*, 1991) of the geometries of unsubstituted and substituted (Allen *et al.*, 1995) aromatic amines. However, later *ab initio* studies performed on the aniline free molecule (Adams, 1993; Bludsky *et al.*, 1996) and the determination of the structures of 2- and 3-aminophenols by neutron diffraction (Allen, Hoy *et al.*, 1997) have provided some evidence of non-planarity. On the other hand, Ferretti *et al.* (1993) have found a correlation between the planarity of the group and the degree of double-bond character of the C—NH$_2$ bond. Besides, semi-empirical calculations performed on *p*- and *m*-aniline clusters, which take into account the non-planarity of the group, indicate that aggregation results in complete planarity of the amino group (Turi & Dannenberg, 1996).

Intramolecular charge transfer and cooperativity of the molecular interactions could be claimed to explain the chain formation and molecular assembly, and the

different degrees of amino planarity in nitroanilines. The only available data, which come from an experimental charge-density analysis carried out using high-angle X-ray single-crystal diffraction data collected on 2-methyl-4-nitroaniline (2M4NA) (Howard *et al.*, 1992), seem to supply evidence of non-planarity, but the quality of the crystal used was not high enough to make this study conclusive. 2M4NA has been the subject of numerous experimental and theoretical investigations because it exhibits an exceptionally large linear electro-optic effect (Lipscomb *et al.*, 1981) and second-harmonic coefficient (Levine *et al.*, 1979). Solution UV spectra (Ellena, Punte & Rivero, 1996) and X-ray data (Howard *et al.*, 1992) show that 2M4NA is a highly conjugated molecule and that its crystal packing shows a hydrogen-bond scheme that follows the description of Etter *et al.* (1990).

Solution UV and room-temperature X-ray single-crystal studies of the isomeric 2-methyl-5-nitroaniline (2M5NA) (Ellena, Punte & Rivero, 1996) have shown a smaller degree of molecular conjugation than 2M4NA with a similar chain motif, despite the presence of hydrogen-bonded centrosymmetric dimers which rules against non-centric packing, and possible non-conventional hydrogen bonds stabilizing its three-dimensional structure. To clarify the relationship between the different parameters which appear to influence the self-assembly of nitroanilines, reliable H-atom positions must be obtained. Therefore, a single-crystal neutron diffraction study of a large high-quality crystal of 2M5NA has been performed. The aim of this study is to establish the degree of planarity of the amino group and to add to the understanding of the role of the hydrogen bonds in the molecular organization of nitroanilines. In addition, the reliable H-atom positions thus obtained can be the starting point either for an electron distribution study or for aggregate calculations that would allow the reliability of the additivity model to be checked.

2. Experimental

The compound, purchased from a commercial source (Janssen), was purified and recrystallized by cooling to room temperature a hot saturated solution in benzene and then a hot saturated solution in methanol. The product obtained, an orange polycrystalline powder, was used to grow a crystal of approximate dimensions $15 \times 6 \times 3$ mm by slow evaporation of a methanol solution. A fragment of this crystal with dimensions $5 \times 3 \times 2$ mm was used for the neutron diffraction experiment. Neutron diffraction data were collected on the SXD instrument at the ISIS spallation neutron source using the time-of-flight Laue diffraction method (Wilson, 1997). Two position-sensitive detectors, each with an active area of 192×192 mm in 3×3 mm pixels, were used. These were situated with their centres at $2\theta =$

Table 1. *Experimental details*

Crystal data	
Chemical formula	$C_7H_8N_2O_2$
Chemical formula weight	152
Cell setting	Monoclinic
Space group	$P2_1/n$
a (Å)	9.369 (2)
b (Å)	5.563 (1)
c (Å)	13.626 (3)
β (°)	92.36 (3)
V (Å^3)	709.6 (2)
Z	4
D_x (Mg m^{-3})	1.423
Radiation type	Neutron
Wavelength range (Å)	0.5–5
No. of reflections for cell parameters	120
μ (mm^{-1})	$0.093 + 0.089\lambda$ (where λ is in Å)
Temperature (K)	100 (2)
Crystal form	Irregular prism
Crystal size (mm)	$5 \times 3 \times 2$
Crystal colour	Orange
Data collection	
Radiation source	ISIS
Diffractometer	SXD
Data collection method	Time-of-flight Laue diffraction
Absorption correction	Empirical
T_{min}	0.47
T_{max}	0.85
No. of measured reflections	17 278
No. of independent reflections	3386
No. of observed reflections	3386
Criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	0.0600
θ_{max} (°)	21.5
Range of h, k, l	$0 \rightarrow h \rightarrow 24$
	$0 \rightarrow k \rightarrow 13$
	$-30 \rightarrow l \rightarrow 27$
Refinement	
Refinement on	F^2
$R[F^2>2\sigma(F^2)]$	0.0669
$wR(F^2)$	0.1544
S	1.137
No. of reflections used in refinement	3386
No. of parameters used	172
H-atom treatment	All H-atom parameters refined
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.1119P)^2 + 1.3458P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	-0.001
Extinction method	Becker & Coppens (1974) Lorentzian model
Extinction coefficient (rad^{-1})	0.325×10^{-4}
Source of neutron scattering lengths	*International Tables for Crystallography* (1992, Vol. C, Table 4.4.4.1)

$52.5°$, $\sim$203 mm from the sample (low-angle detector), and $2\theta = 123°$, $\sim$145 mm from the sample (high-angle detector). The crystal, attached to an aluminium pin by two aluminium adhesive strips, was mounted on a two-

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($\mathring{A}^2$)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
C1	1.00918 (9)	0.1891 (2)	0.29213 (8)	0.00944 (14)
C2	0.96433 (9)	−0.0194 (2)	0.23937 (7)	0.00990 (14)
C3	0.86971 (10)	−0.1782 (2)	0.28168 (8)	0.0116 (2)
C4	0.81377 (10)	−0.1356 (2)	0.37340 (8)	0.01124 (15)
C5	0.85647 (9)	0.0742 (2)	0.42127 (7)	0.00891 (13)
C6	0.95266 (9)	0.2355 (2)	0.38383 (7)	0.00968 (14)
C7	1.01863 (11)	−0.0674 (2)	0.13949 (9)	0.0164 (2)
N1	1.10806 (9)	0.34293 (15)	0.25496 (7)	0.01679 (15)
N2	0.79435 (7)	0.13194 (13)	0.51505 (6)	0.01191 (12)
O1	0.6994 (2)	0.0025 (3)	0.54424 (12)	0.0237 (3)
O2	0.8377 (2)	0.3094 (3)	0.56024 (11)	0.0207 (3)
H3	0.8379 (3)	−0.3399 (5)	0.2419 (2)	0.0298 (6)
H4	0.7401 (3)	−0.2593 (5)	0.4065 (2)	0.0314 (6)
H6	0.9826 (3)	0.3960 (5)	0.4244 (2)	0.0281 (5)
H11	1.1247 (3)	0.5013 (5)	0.2891 (3)	0.0329 (6)
H12	1.1320 (3)	0.3373 (6)	0.1841 (2)	0.0324 (6)
H71	1.1340 (3)	−0.0916 (8)	0.1416 (3)	0.0405 (8)
H72	0.9955 (5)	0.0843 (7)	0.0895 (3)	0.0425 (8)
H73	0.9713 (4)	−0.2277 (7)	0.1067 (3)	0.0407 (8)

Table 3. *Selected geometric parameters ($\mathring{A}$, °)*

C1—N1	1.3734 (11)	C5—N2	1.4615 (12)
C1—C6	1.4011 (13)	C6—H6	1.081 (3)
C1—C2	1.4187 (13)	C7—H71	1.088 (3)
C2—C3	1.3934 (13)	C7—H72	1.101 (4)
C2—C7	1.4964 (15)	C7—H73	1.084 (3)
C3—C4	1.3953 (15)	N1—H11	1.006 (3)
C3—H3	1.086 (3)	N1—H12	1.001 (3)
C4—C5	1.3878 (14)	N2—O1	1.2235 (15)
C4—H4	1.086 (3)	N2—O2	1.224 (2)
C5—C6	1.3840 (12)		
N1—C1—C6	119.95 (9)	C5—C6—C1	119.00 (8)
N1—C1—C2	120.85 (8)	C5—C6—H6	120.4 (2)
C6—C1—C2	119.19 (8)	C1—C6—H6	120.6 (2)
C3—C2—C1	119.27 (9)	C2—C7—H71	111.9 (2)
C3—C2—C7	120.60 (9)	C2—C7—H72	111.1 (2)
C1—C2—C7	120.13 (9)	H71—C7—H72	106.3 (3)
C2—C3—C4	122.11 (9)	C2—C7—H73	111.9 (2)
C2—C3—H3	119.0 (2)	H71—C7—H73	107.3 (3)
C4—C3—H3	118.9 (2)	H72—C7—H73	108.0 (4)
C5—C4—C3	116.90 (8)	C1—N1—H11	118.0 (2)
C5—C4—H4	120.9 (2)	C1—N1—H12	121.2 (2)
C3—C4—H4	122.2 (2)	H11—N1—H12	116.0 (3)
C6—C5—C4	123.47 (9)	O1—N2—O2	122.79 (11)
C6—C5—N2	117.95 (8)	O1—N2—C5	118.42 (10)

circle goniometer (φ, χ) in a Displex closed-cycle-refrigerator helium cryostat. Data were collected at a temperature of 100 (2) K. The computer-controlled temperature was measured by an Rh–Fe thermocouple positioned around 10 mm from the sample at the closed-cycle-refrigerator head. A total of 42 frames were collected, each containing information from the two detectors with an exposure time for each frame of around 3 h. The precise exposure time depended on the neutron flux per hour with the crystal exposed to the same total neutron flux in each frame.

The intensities were extracted and reduced to structure factors using standard SXD procedures (Wilson, 1997), and structure refinement was carried out using *SHELXL*93 (Sheldrick, 1993). All non-H-atom positions from the X-ray model were used as a starting point for the refinement. H atoms were located from subsequent difference Fourier maps. All atoms were refined with anisotropic displacement parameters. Crystal data and a summary of the data collection and refinement parameters are given in Table 1 and the structure is shown in Fig. 1†.

3. Results and discussion

Final atomic coordinates and intramolecular distances for all atoms are displayed in Tables 2 and 3, respectively. The analysis of the molecular geometry shows some differences from the X-ray single-crystal structure determination. The amino and nitro groups present rotations out of the mean ring plane of 19.3 (3) and

6.5 (2)°, respectively, larger than those in the X-ray structure [3.7 (20) and 3.3 (3)°]. However, the degree of molecular conjugation inferred from UV spectra in solution seems to be sustained, as can be assessed by the invariance, within 3σ, of C1—N1 [1.373 (1) $\mathring{A}$] and C5—N2 [1.461 (1) $\mathring{A}$]. The corresponding bond lengths for the X-ray structure are 1.369 (2) and 1.468 (5) $\mathring{A}$, respectively.

The aromatic ring shows a slight departure from planarity; a boat deformation with the C1 and C6 atoms out of the mean plane (MP_{Ph}) defined by the other ring C(aryl) atoms by −0.046 (1) and −0.032 (1) $\mathring{A}$, respec-
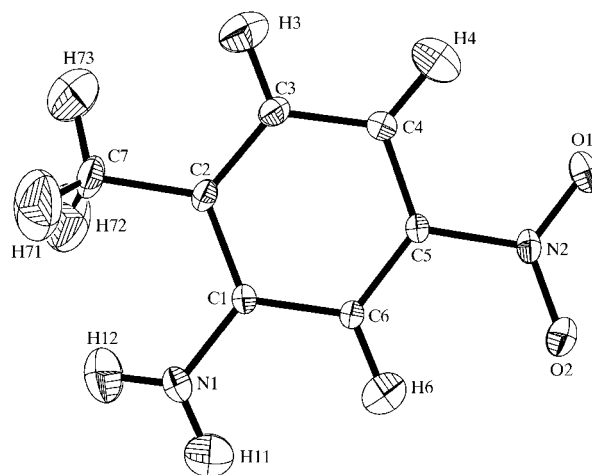

Fig. 1. A 70% probability displacement-ellipsoid plot of 2M5NA showing the numbering scheme.

tively, is present. The total puckering amplitude Q_T (Cremer & Pople, 1975), 0.024 (2) Å, is more pronounced than that obtained from the X-ray molecular geometry [0.014 (4) Å]. The observed deviations of some of the geometrical parameters from those obtained in the X-ray structure determination, mainly those involving H atoms, were expected because neutrons are scattered by atomic nuclei while X-rays are scattered by electrons. However, this cannot account for geometrical discrepancies related to the NO_2 group. These could be a consequence of the different temperatures at which the data collections were performed. The existence of librational and/or occupational disorder of the nitro group in nitrobenzene derivatives has been known for a long time (Mak & Trotter, 1965; Gopal *et al.*, 1980). The temperature at which the neutron data were collected, 100 K, could have frozen the otherwise feasible internal librations of the nitro group. Thermal-motion analysis confirms this assumption.

The planarity of the amino group was analyzed, following Ferretti *et al.* (1993), through the examination of the two internal coordinates τ and χ_N shown in the scheme below.
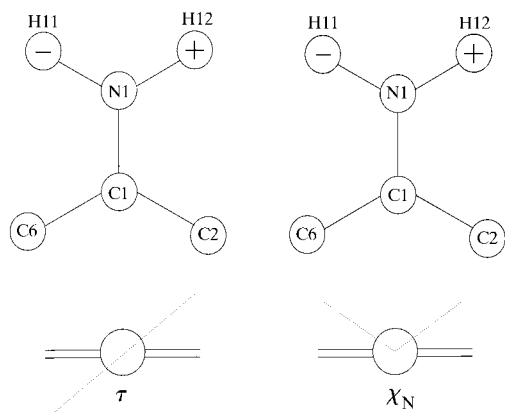
These are functions of the torsion angles involving the H atoms: $\omega_1 = $ C6—C1—N1—H11 $= 10.7$ (3)°, $\omega_2 = $ C2—C1—N1—H12 $= -15.9$ (2)°; $\omega_3 = $ C2—C1—N1—H11 $= -170.1$ (2)° and $\omega_4 = $ C6—C1—N1—H12 $= 164.9$ (2)°. τ [$(0 \le \tau \le 90°) = (\omega_1 + \omega_2)/2$] characterizes the rotation around the C1—N1 bond and χ_N [$(0 \le \chi_N \le 60°) = \omega_2 - \omega_3 + \pi(\text{mod }2\pi)$] is a measure of the degree of the N-atom pyramidalization (P_N). The extreme values, 0 and 60°, correspond to a planar sp^2 and a regular tetrahedral sp^3 hybridized N atom, respectively. The values obtained in the present work, $\tau = 2.6$ (5)° and $\chi_N = 25.8$ (4)°, indicate a slight rotation and a significant P_N. P_N can also be assessed from the distance of the N atom to the plane made by its substituents (H11, H12, C1) [0.142 (2) Å], the angle formed by the C1—N1 bond and the plane MP$_{Ph}$ [3.05 (7)°] and the sum of the angles about the amino-N atom [355.1 (7)°]. The partial amino-group planarity has been related to intermolecular

Table 4. *Hydrogen-bonding geometry (Å, °)*

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H12$\cdots$O1[i]	1.001 (3)	2.219 (4)	3.149 (2)	154.0 (3)
N1—H12$\cdots$O2[i]	1.001 (3)	2.738 (4)	3.585 (2)	142.7 (3)
N1—H11$\cdots$O1[ii]	1.004 (3)	2.321 (3)	3.199 (2)	145.3 (3)
C3—H3$\cdots$C(Ph)[iii]	1.085 (3)	2.608 (3)	3.414 (1)	130.5 (2)
C4—H4$\cdots$O1	1.086 (3)	2.418 (4)	2.713 (2)	93.7 (2)
C6—H6$\cdots$O2	1.081 (3)	2.389 (3)	2.706 (2)	94.9 (2)
C6—H6$\cdots$O2[ii]	1.081 (3)	2.353 (3)	3.275 (2)	142.2 (2)
C7—H71$\cdots$O2[i]	1.088 (3)	2.740 (4)	3.525 (2)	128.8 (3)
C7—H71$\cdots$O1[iv]	1.088 (3)	2.725 (4)	3.255 (2)	109.5 (3)
C7—H73$\cdots$O1[iv]	1.084 (3)	2.789 (4)	3.255 (2)	105.8 (2)

Symmetry codes: (i) $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $2 - x, 1 - y, 1 - z$; (iii) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iv) $\frac{1}{2} + x, -\frac{1}{2} - y, z - \frac{1}{2}$.

interactions inducing cooperative effects. Therefore, the intermolecular interactions were analyzed carefully.

The intermolecular distances suggest that different types of hydrogen bonds are present (Fig. 2 and Table 4). The H12 amino-H-atom position and distances to the O[i] atoms [symmetry code: (i) $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$] indicate, in accordance with Panunto *et al.* (1987), that it is connected to the two O atoms of a nitro group through a bifurcated hydrogen bond. The geometry of C—nitro-O$\cdots$H—N hydrogen bonds has recently been reviewed by Allen, Baalham *et al.* (1997). They performed a combined database study and *ab initio* molecular-orbital calculations of the two principal motifs observed in crystal structures (Allen, Lommerse *et al.*, 1997): bifurcated [either symmetric, (I) or asymmetric, (II)] and monocoordinated [(III)], as shown in the scheme below.
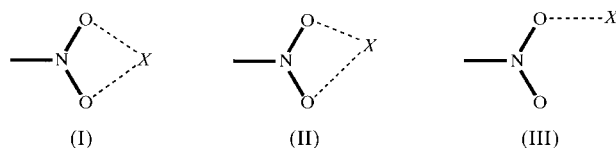
From it, they concluded that there is a preference for a strongly asymmetric bifurcated motif (II) with donors approaching the nitro-O atoms in the C—NO_2 planes.

Comparison of the present results with the mean values obtained from the study of Allen, Baalham *et al.* (1997) shows that 2M5NA presents motif (II). The H$\cdots$acceptor distance, 2.219 (2) Å, is shorter than the mean [2.26 (1) Å] and the interaction is more directional with a donor—H$\cdots$acceptor (D—H$\cdots A$) angle of 154.0 (3)° [mean 145.9 (12)°]. It should be mentioned that the D—H$\cdots A$ angle is close to the peak value for the moderate and weak hydrogen-bond angle distribution curve, ~155° according to Jeffrey (1997). The H12 atom, within experimental error, lies in the plane defined by the nitro group and the approaching angle to the direction defined by O1[i]—N2[i] is 106.2 (1)°. This value would indicate either a strong H12$\cdots$O2[i] interaction, which is not supported by the H12$\cdots$O2[i] distance [2.738 (4) Å], or a distortion of the expected O2 lone-pair direction. As seen already from the X-ray data, this

N—H···O(nitro) interaction links molecules related by a glide plane and induces the formation of infinite polar chains along [10$\bar{1}$], where consecutive molecules are rotated by 60.15 (4)°. Molecules in the chain are also joined by a weak C(methyl)—H···O^i interaction, depicted in Fig. 2.

The analysis of the intermolecular interactions also shows that molecules related by an inversion centre [symmetry code (ii)] are linked by four hydrogen bonds (see Fig. 2), which generate centrosymmetric dimers. Two of the hydrogen bonds involve the amino-H atom H11 and O2; the other two hydrogen bonds, previously unrecognized, connect the aromatic H atom H6 with the same O atom. This means that two intermolecular six-membered hydrogen-bond rings (Bernstein *et al.*, 1994) link two aromatic systems. Therefore, some degree of resonance can be assumed to further stabilize the dimeric units (Jeffrey, 1997). So, by combining the interactions described above, two adjacent antiparallel chains are linked by the centrosymmetric dimer interactions. This gives rise to non-polar ribbons (see Fig. 3) which inhibit the macroscopic second-order non-linear optical response of 2M5NA.

It was concluded from the X-ray results (Ellena, Punte & Rivero, 1996) that chain development, even in the presence of dimeric units, reinforced the assumption of Panunto *et al.* (1987) that the N—H···O(nitro) synthons in nitroanilines are so strong they overcome other interactions, inducing molecules to assemble in chains as the first aggregation step in solution. The present results bring some doubts about this assertion. Comparison of the interactions that give rise to the chains with those that induce the dimeric arrangement suggests that in 2M5NA the short-range ordering (dimer formation) is energetically more stable than the long-range ordering (chain development). This is supported by the melting point of 2M5NA, 378 (2) K, which is lower than that of 2M4NA [405 (1) K]. In the latter, long-range ordering prevails, chains are connected head-to-head and dimeric units are not observed.

The interactions described above do not fully account for the three-dimensional arrangement of the 2M5NA molecules. Moreover, comparison of the packing of 2M5NA, 2M4NA and *m*-nitroaniline (mNA) (the last two acentric but showing noticeable differences) indicates that 2M4NA and mNA molecules belonging to the same chain are coplanar. Hence the analysis of causes of the rotation of consecutive molecules in 2M5NA chains might shed light on molecular assembling preferences. A close examination of the interactions between the ribbons was undertaken to provide evidence for the various competitive intermolecular forces at play. It was found that the ribbons along the [10$\bar{1}$] direction are interlinked with equivalent ribbons along the *b* axis, forming (101) layers (Fig. 4). The interactions which link these ribbons are the centrosymmetric dimer interaction and the two weak C(methyl)—H···O^{iv} interactions shown in Fig. 2 and described in Table 4.

Another, non-conventional, hydrogen bond was also found. The aromatic H atom H3 is at a short distance, 2.608 (3) Å, from the centre of an aromatic ring, C_{Ph}, of a molecule related by symmetry operation (iii) ($\frac{3}{2} - x$, $y - \frac{1}{2}$, $\frac{1}{2} - z$). The H···C_{Ph}^{iii} distance is shorter than any H···C(aryl)^{iii} distance although the C3—H3 bond does
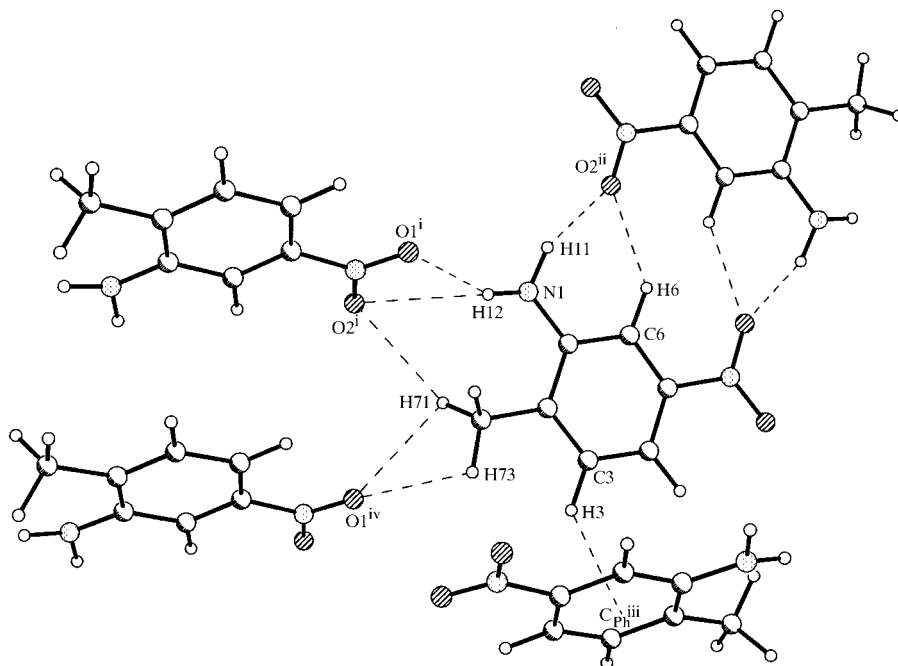

Fig. 2. An illustration of the intermolecular hydrogen-bonding pattern in 2M5NA.

not point to C_{Ph}^{iii}. Fig. 2 displays the geometry of this hydrogen bond, which involves an aromatic H atom and the π cloud of a neighbouring ring rotated by 60.15 (4)° and belonging to an adjacent layer. Fig. 4 illustrates this interlayer interaction.

It has been found that C—H···X, mainly C—H···O, hydrogen bonds determine crystal packing when stronger hydrogen bonds are absent (Desiraju, 1996). However, some of the features of the packing of organic molecules (including nitroanilines) can not be explained without taking into account the C—H···X and the 'aromatic' X—H···π interactions even when stronger hydrogen bonds are at play. In particular, C6—H6···O(nitro) interactions have been found to be a recurrent motif that might determine molecular organization in 2,4-dinitroanilines (Ellena *et al.*, 1997) and 2,4-dinitrobenzenes (Ellena, Punte & Nudelman, 1996). Much effort has been dedicated recently to the characterization of X—H···π bonds. Neutron diffraction studies have shown the existence of N—H···π bonds in 2- and 3-aminophenols (Allen, Hoy *et al.*, 1997) and of C(ethynyl)···π bonds in 5-ethynyl-5H-dibenzo[a,d]-cyclohepten-5-ol at 20 K (Steiner *et al.*, 1997). C(aryl)—H···π interactions, like those found in 2M5NA, are more unusual and weaker than the ones mentioned above, and they have been the subject of considerable controversy.

The relative influence of the different hydrogen-bond interactions depicted above is difficult to assess from the present results. The structure of 2M5NA shows the coexistence of the two packing motifs usually preferred by aromatic molecules: herringbone, assigned by some authors to a coulombic C(aryl)—H···π attraction (Gavezzotti, 1994; Desiraju, 1989, and references therein), and stacking, induced by core–core interactions (Gavezzotti, 1994). A stacking motif can be recognized within the non-polar layers, while the observed C3—H3···π interaction can explain the assembly of the layers. The C3—H3···π interaction may even be the cause of the rotation of consecutive molecules in the chain that favours the dimer formation and impairs the ordering of single stacks observed in many nitrobenzenes (André *et al.*, 1997*a*) and the head-to-head alignment of the chains. However, its driving force is not strong enough to induce either any of the long-range herringbone motifs that are described in the literature (Desiraju, 1989, and references therein) or the nitrobenzene pseudo-herringbone packing mode recently depicted by André *et al.* (1997*b*). Cooperativity of the hydrogen-bond interactions in the chain could neither be supported nor denied from the present results. Charge-density analyses and *ab initio* calculations of 2M5NA in progress will explore further the possibility of predicting crystal packing and macroscopic properties from known molecular structures.

4. Conclusions

The single-crystal neutron diffraction study of 2-methyl-5-nitroaniline has provided conclusive evidence that the amino group adopts an appreciable degree of non-planarity. This is contrary to expectations based on aggregate calculations performed on other systems with similar molecular conjugation and chain patterns. We emphasize that the observed intermolecular interactions, even the very weak ones like C(aryl)—H···π which may be responsible for the differences in geometry of the N—H···O(nitro)-mediated chains in the two isomers 2M5NA and 2M4NA, should be taken into account when seeking connections between mole-
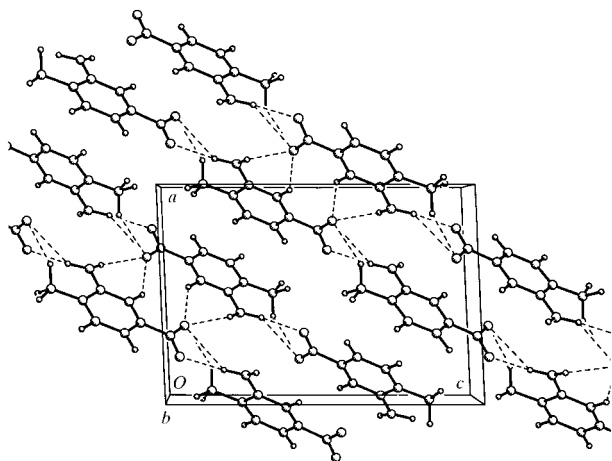

Fig. 3. A view of 2M5NA along the b axis, showing the antiparallel polar chains forming the non-polar ribbons along [10$\bar{1}$] and the intermolecular hydrogen bonds involved in the formation of these chains and ribbons.
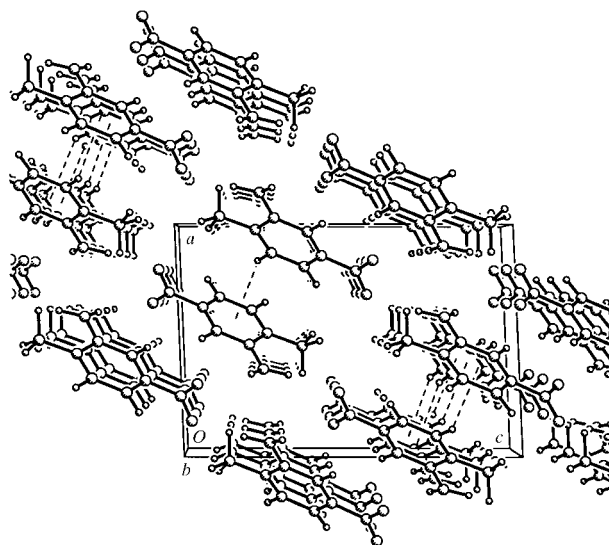

Fig. 4. A view of 2M5NA along the b axis, showing the (101) layers and the C3—H3···π interaction linking them.

cular and supramolecular geometries and crystal packing.

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