

# Influence of hydrogen bonding on the second harmonic generation effect: neutron diffraction study of 4-nitro-4'-methylbenzylidene aniline

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A neutron diffraction study of the non-linear optical (NLO) material 4-nitro-4'-methylbenzylidene aniline (NMBA) is presented. NMBA exhibits a large macroscopic second-order NLO susceptibility,  $\chi^{(2)}$ , and this study shows that hydrogen bonding is, in part, responsible for this. No hydrogen bonding was reported in the X-ray study [Ponomarev *et al.* (1977). *Sov. Phys. Crystallogr.* **22**, 223–225], whereas the present work shows that C–H $\cdots$ X hydrogen bonds (where X = N, O or  $\pi$ ) direct the nature of the three-dimensional lattice. C–H $\cdots$ X (X = N or O) hydrogen bonds are common; however, C–H $\cdots$  $\pi$  hydrogen-bond motifs are relatively rare. Such intermolecular interactions help extend the molecular charge transfer into the supramolecular realm, the charge transfer originating as a consequence of the high level of molecular planarity and strong donor-to-acceptor interactions. Molecular planarity, coupled with the favourable nature of the hydrogen bonds, results in parallel stacking of molecules in both the *a* and *c* crystallographic directions with extremely close interplanar spacings. Such a combination of influential hydrogen-bonding characteristics accounts, in part, for the large second-order NLO output of the material since the phenomenon is so critically dependent upon the nature of the charge transfer.

## 1. Introduction

Organic non-linear optical (NLO) materials have shown great promise in the optoelectronic and telecommunication industries over recent years (Fejer, 1994; Zyss, 1994; Burland, 1994; Long, 1995). In particular, measurements of the second-order NLO effect, second-harmonic generation (SHG), on certain organic NLO compounds have already produced results that by far exceed those obtained from all known inorganic NLO alternatives (Chemla & Zyss, 1987), *e.g.* LiNbO<sub>3</sub>. Moreover, organic materials generally have significantly higher optical thresholds and much greater versatility in molecular design compared with their inorganic counterparts, thereby providing many more opportunities for improving the SHG response (Long, 1995, and references therein).

SHG is one of the most important aspects of NLO research since it lends itself to a myriad of applications: from telecommunications to visible light lasers, through to surface-enhanced Raman spectroscopy (Fejer, 1994; Zyss, 1994; Burland, 1994; Long, 1995). The level of SHG response of a given material is inherently dependent upon its structural attributes. On a molecular scale, the extent of charge transfer (CT) across the NLO chromophore determines the level of SHG output (Davydov *et al.*, 1970; Oudar & Zyss, 1982; Oudar,

1977; Lalama & Garito, 1979; Albrecht & Morell, 1979): the greater the CT, the larger the SHG output. The presence of strong intermolecular interactions, such as hydrogen bonds, can extend this level of CT into the supramolecular realm, owing to their electrostatic and directed nature, thereby enhancing the SHG response. In the absence of large steric hindrance, the nature of such interactions together with the molecular CT effects, generally dictate the type of molecular packing environment. Extensive CT *within* a molecule generally favours centrosymmetric packing since such effects induce large molecular dipoles which tend to oppose each other. However, the presence of CT *between* molecules through hydrogen bonding will generally favour a head-to-tail (non-centrosymmetric) arrangement of molecules. SHG is only observed in non-centrosymmetric materials since the phenomenon is a third-rank tensor (Cady, 1946). A delicate balance between CT effects and the nature of the intermolecular interactions must therefore be achieved in order to obtain optimal SHG-active materials. For use in practical applications, such materials should ideally also be phase-matchable (Franken & Ward, 1963), although periodic domain-inversion techniques (Armstrong *et al.*, 1962) are being developed (Hu *et al.*, 1996) to overcome this requirement. In the monoclinic crystal system (to which the present crystal structure belongs), the associated phase-matching angle,  $\theta_{\text{PM}}$ , is defined as the angle between the charge-transfer axis of the molecule and the crystallographic screw axis that generates the herringbone structure, and its optimal value is  $54.74^\circ$ , as derived by Oudar & Zyss (1982).

Bearing these factors in mind, we became intrigued by the compound 4-nitro-4'-methylbenzylidene aniline (NMBA). Two polymorphs of the compound are known: a triclinic form and a monoclinic form (Ponomarev *et al.*, 1977). Whilst the triclinic form ( $P\bar{1}$ )<sup>1</sup> is SHG-inactive on account of its centrosymmetry, the monoclinic form ( $Pc$ ) of NMBA exhibits an SHG output (Bailey *et al.*, 1993; Tsunekawa *et al.*, 1990) of between 16 and 27 times that of urea,<sup>2</sup> the standard reference material. The attractive structural characteristics of NMBA, on the molecular scale, are: extensive  $\pi$ -conjugation, good planarity, and strong electron donor and acceptor groups at opposite ends of the molecule; and yet, whilst the original X-ray diffraction report revealed NMBA to have a non-centrosymmetric structure, no other favourable NLO features, on the supramolecular scale, were discerned. In particular, there was no report of any hydrogen bonding in the original X-ray diffraction study (Ponomarev *et al.*, 1977). Indeed, several of the H atoms in this study were not even located, but were modelled according to expected geometry. In view of our earlier arguments, the apparent absence of any hydrogen bonding is surprising given the co-existence of crystallographic non-centrosymmetry and evident molecular CT possibilities. Moreover, the compound exhibits this high SHG activity despite having a poor phase-matching ability, as deduced from

<sup>1</sup> Cell parameters:  $a = 12.561$  (7),  $b = 14.372$  (5),  $c = 7.108$  (5) Å,  $\alpha = 96.02$  (5),  $\beta = 93.72$  (5),  $\gamma = 72.65$  (5)°,  $Z = 4$ .

<sup>2</sup> The wide range reported arises from a variety of disparate experimental reports.

**Table 1**  
Experimental details.

Crystal data	
Chemical formula	$\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_2$
Chemical formula weight	240
Cell setting, space group	Monoclinic, $Pc$
$a, b, c$ (Å)	7.305 (4), 11.495 (5), 7.240 (3)
$\beta$ (°)	109.71 (5)
$V$ (Å <sup>3</sup> )	572.3 (5)
$Z$	2
$D_x$ (Mg m <sup>-3</sup> )	1.393
Radiation type	Neutron
Wavelength (Å)	1.26170
No. of reflections for cell parameters	1349
$\theta$ range (°)	15.40–70.40
$\mu$ (mm <sup>-1</sup> )	0.18
Temperature (K)	20.0 (1)
Crystal form, colour	Block, yellow
Crystal size (mm)	$5.3 \times 2.1 \times 1.2$
Data collection	
Diffractometer	D10
Data collection method	$\omega$ - $x$ - $\theta$ scans
Absorption correction	Integration (Coppens, 1970)
$T_{\text{min}}$	0.6175
$T_{\text{max}}$	0.8055
No. of measured, independent and observed parameters	1877, 1349, 1304
Criterion for observed reflections	$I > 2\sigma(I)$
$R_{\text{int}}$	0.0169
$\theta_{\text{max}}$ (°)	70.40
Range of $h, k, l$	$-4 \rightarrow h \rightarrow 10$ $-16 \rightarrow k \rightarrow 16$ $-10 \rightarrow l \rightarrow 10$
No. and frequency of standard reflections	1 every 50 reflections
Refinement	
Refinement on	$F^2$
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.0306, 0.0469, 1.995
No. of reflections and parameters used in refinement	1349, 272
H-atom treatment	All H-atom parameters refined
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0000P)^2 + 0.0000P]$ , where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}}$	-0.002
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.516, -0.503
Extinction method	SHELXL93 (Sheldrick, 1993)
Extinction coefficient	0.0071 (6)

Computer programs used: *MAD* (Barthelemy, 1984), *RAFIN COLL5N* (Lehmann & Wilson, 1987), *SHELXS86* (Sheldrick, 1990), *SHELXL93* (Sheldrick, 1993), *SHELXTL-Plus* (Sheldrick, 1995).

the phase-matching angle,  $\theta_{\text{PM}}$ , of  $72.88^\circ$  (Bailey *et al.*, 1993), which is far from the optimal  $54.74^\circ$  for a monoclinic system (Oudar & Zyss, 1982).

We were therefore keen to establish:

(i) whether or not there really were any hydrogen bonds present within the lattice that overcome the molecular CT effects to enforce this non-centrosymmetry and

(ii) why a notable SHG output is observed despite the non-optimal phase-matching angle.

The structural study on NMBA reported herein was carried out in order to investigate these matters, neutron diffraction being the chosen technique since it provides the most reliable determination of hydrogen positions, and thence the precise characterization of any hydrogen bonds.

**Table 2**

Bond lengths for the 20 K neutron-derived structure of NMBA.

O(1)—N(2)	1.233 (2)	C(7)—H(7)	1.093 (6)
O(2)—N(2)	1.216 (3)	C(8)—C(9)	1.397 (3)
N(1)—C(7)	1.278 (2)	C(8)—C(13)	1.405 (3)
N(1)—C(8)	1.420 (3)	C(9)—C(10)	1.394 (3)
N(2)—C(5)	1.464 (3)	C(9)—H(9)	1.091 (5)
C(1)—C(6)	1.396 (3)	C(10)—C(11)	1.402 (3)
C(1)—C(2)	1.401 (3)	C(10)—H(10)	1.093 (6)
C(1)—H(1)	1.078 (6)	C(11)—C(12)	1.402 (3)
C(2)—C(3)	1.402 (3)	C(11)—C(14)	1.502 (4)
C(2)—C(7)	1.471 (3)	C(12)—C(13)	1.390 (3)
C(3)—C(4)	1.387 (4)	C(12)—H(12)	1.089 (5)
C(3)—H(3)	1.083 (4)	C(13)—H(13)	1.091 (6)
C(4)—C(5)	1.390 (3)	C(14)—H(14A)	1.081 (6)
C(4)—H(4)	1.088 (6)	C(14)—H(14B)	1.093 (4)
C(5)—C(6)	1.389 (3)	C(14)—H(14C)	1.084 (7)
C(6)—H(6)	1.095 (5)		

**Table 3**

Selected bond angles for the 20 K neutron-derived structure of NMBA.

C(7)—N(1)—C(8)	120.9 (1)	C(4)—C(5)—N(2)	118.8 (2)
O(2)—N(2)—O(1)	123.5 (2)	N(1)—C(7)—C(2)	121.6 (2)
O(2)—N(2)—C(5)	118.8 (2)	N(1)—C(7)—H(7)	123.0 (3)
O(1)—N(2)—C(5)	117.7 (2)	C(2)—C(7)—H(7)	115.3 (3)
C(2)—C(1)—H(1)	120.0 (4)	C(9)—C(8)—N(1)	125.3 (2)
C(6)—C(1)—H(1)	119.8 (3)	C(13)—C(8)—N(1)	116.4 (2)
C(1)—C(2)—C(7)	118.7 (2)	C(10)—C(11)—C(14)	120.9 (2)
C(3)—C(2)—C(7)	121.6 (2)	C(12)—C(11)—C(14)	121.3 (2)
C(6)—C(5)—N(2)	118.5 (2)		

## 2. Experimental

The Cu(200) monochromated [ $\lambda = 1.2617(3) \text{ \AA}$ ] four-circle neutron diffractometer, D10, at the Institut Laue Langevin (ILL), Grenoble, France, equipped with a liquid helium cryostat (Zeyen *et al.*, 1984), was employed for this study. Experimental details are given in in Table 1.<sup>3</sup>

## 3. Results and discussion

A 50% probability thermal ellipsoid plot of the neutron derived structure is shown in Fig. 1 and its three-dimensional arrangement within the lattice is illustrated in Fig. 2. Bond lengths and selected bond angles are given in Tables 2 and 3, respectively.

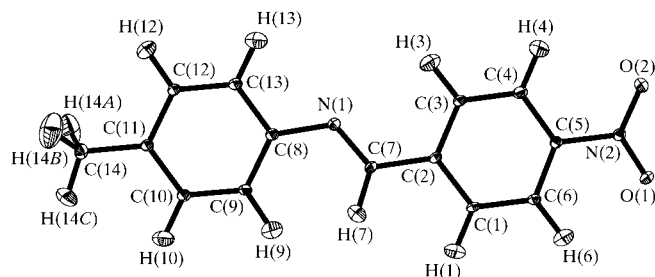
The two aromatic rings in the molecule are linked *via* a —CH=N— moiety and each ring is twisted relative to the other by  $3.9(1)^\circ$ .<sup>4</sup> The twist angle of each phenyl ring relative to the mean plane of the molecule is  $2.6(1)^\circ$  [C(1)—C(6)] and

<sup>3</sup> Supplementary data for this paper are available from the IUCr electronic archives (Reference: AN0580). Services for accessing these data are described at the back of the journal.

<sup>4</sup> In contrast, the aromatic rings in the triclinic polymorph of NMBA are considerably twisted [the aniline/benzylidene ring in molecules (I) and (II) ( $Z' = 2$ ) being, respectively,  $40.2/13.1$  and  $28.5/4.2^\circ$  relative to the C—N=CH=C branch]; such a twist represents the principal molecular difference between the two polymorphs (Ponomarev, 1977).

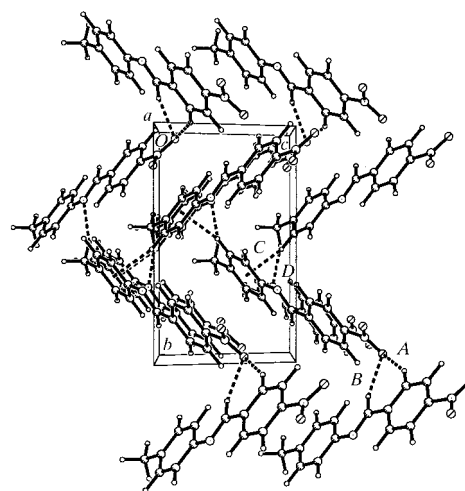
$1.3(1)^\circ$  [C(8)—C(13)]. The nitro group deviates from the mean plane of the molecule by  $12.2(1)^\circ$ . The molecule is therefore almost completely planar. The high degree of planarity correlates with the high degree of  $\pi$ -conjugation throughout the molecule. This, in turn, enhances the methyl-nitro donor–acceptor interactions across the molecule and hence, the degree of molecular CT.

Significant molecular CT effects might be expected to cause a perturbation of formally aromatic rings towards a more quinoidal electronic configuration since this provides a more extended level of  $\pi$ -conjugation in the system (Marder & Perry, 1993). The molecular geometry observed does indeed suggest such a tendency towards quinoidal character, in that the bonds C(1)—C(6), C(3)—C(4), C(9)—C(10) and C(12)—C(13) are generally shorter than the other C—C bonds in each ring. Despite the fact that the bond length differences are small and at the  $3\text{--}6\sigma$  level, they do tend towards such bond



**Figure 1**

A 50% probability thermal ellipsoid plot of the neutron-derived structure of NMBA.



**Figure 2**

The molecular packing arrangement of the 20 K neutron structure of NMBA as viewed down the *a* axis. The dashed lines represent the C—H...*X* intermolecular hydrogen-bond contacts, *A*, *B*, *C*, *D* [respective hydrogen-bond acceptors and symmetry codes: [O(1)]  $1 + x, 2 - y, \frac{1}{2} + z$ ; [O(1)]  $x - 1, 2 - y, \frac{1}{2} - z$ ; [ $\pi$ (aromatic)]  $x, 1 - y, \frac{1}{2} - z$ ; [N(1)]  $x - 1, 1 - y, \frac{1}{2} - z$ ].

localizations. Additional small variations, resulting from the electron-donating ( $\text{CH}_3$ ) and electron-withdrawing ( $\text{NO}_2$ ) substitution effects in each ring, complicate further the overall polarization of the ring. Neither an aromatic nor a quinoidal description is obvious from the analogous X-ray diffraction results (Ponomarev *et al.*, 1977); indeed, the lack of any pattern at all suggests that the level of accuracy may not have been sufficient to make such a valid assessment in this case.

Four weak intermolecular interactions were located within the three-dimensional lattice of NMBA. All such interactions are of the type  $\text{C}-\text{H}\cdots\text{X}$  (where  $\text{X} = \text{N}, \text{O}$  or  $\pi$ ).  $\text{C}-\text{H}\cdots\text{X}$  interactions were first classified as hydrogen bonds by Taylor & Kennard (1982) and since then have been studied extensively (Desiraju, 1995; Desiraju & Steiner, 1999). Whilst more commonly present in structures where no strong hydrogen-bond donors or acceptors exist (Hoy, 1996), these  $\text{C}-\text{H}\cdots\text{X}$  interactions clearly direct the three-dimensional arrangement of the molecule in NMBA, despite the presence of several oxygen and nitrogen atoms per molecule.

Both of the principal intermolecular interactions,  $\text{C}(1)-\text{H}(1)\cdots\text{O}(1)$  [2.344 (9) Å; 152.2 (4)°; symmetry code:  $1+x, 2-y, \frac{1}{2}+z$ ; *A* in Fig. 2] and  $\text{C}(7)-\text{H}(7)\cdots\text{O}(1)$  [2.380 (8) Å; 153.3 (4)°; symmetry code:  $x-1, 2-y, \frac{1}{2}-z$ ; *B* in Fig. 2], link  $\text{O}(1)$  of one molecule to the  $\text{H}(1)-\text{C}(1)-\text{C}(2)-\text{C}(7)-\text{H}(7)$  moiety of an adjacent molecule, thereby creating a six-membered ring.

The two weaker intermolecular interactions,  $\text{C}(12)-\text{H}(12)\cdots\pi(\text{aromatic})$  [2.58 (1) Å; 156.2 (5)°; symmetry code:  $x, 1-y, \frac{1}{2}-z$ ; *C* in Fig. 2] and  $\text{C}(14)-\text{H}(14\text{A})\cdots\text{N}(1)$  [2.588 (9) Å; 158.5 (4)°; symmetry code:  $x-1, 1-y, \frac{1}{2}-z$ ; *D* in Fig. 2], involve either a  $\pi$  or N hydrogen-bond acceptor. Whilst the latter type of acceptor is very common,  $\text{C}-\text{H}\cdots\pi$  interactions are rare (Viswamitra *et al.*, 1993). Moreover, although  $\text{C}-\text{H}\cdots\pi$  interactions are generally fairly weak, they can be structurally significant (Steiner, 1995*a,b*). In this compound, the  $\pi$  acceptor originates from the centre of the  $\text{C}(8)-\text{C}(13)$  phenyl ring and the corresponding hydrogen bond lies in a direction almost perpendicular to the ring. The  $\text{H}(12)$  atom, to which the  $\pi$  acceptor is linked, therefore lies almost directly below the centre of the ring. The molecule to which the  $\text{H}(12)$  atom is attached lies perpendicular to the molecule containing the  $\pi$  acceptor. This interaction and the contact,  $\text{C}(14)-\text{H}(14\text{A})\cdots\text{N}(1)$ , hold the molecules together along the *b* direction.

The view of the three-dimensional molecular packing arrangement of NMBA, looking down the *a* axis (Fig. 2), shows that molecules translated along the *c* direction pack parallel to each other, as do the molecules translated along the *a* direction. The two parallel stacks of molecules are perpendicular to each other to give the herringbone structure. The mean interplanar spacings between molecules along the *a* and *c* directions are 2.6 (1) and 5.9 (1) Å, respectively. The former distance is extremely short. Moreover, some intermolecular atomic distances lie very close to these values since the parallel molecules pack almost directly on top of each other. Such parallel and close layer-like stacking of molecules is very favourable for the promotion of CT through the lattice. In

turn, this will necessarily aid the level of SHG activity that the material exhibits.

The  $\text{C}-\text{H}\cdots\text{X}$  hydrogen bonding present in NMBA therefore serves a dual role: first, it helps to create the delicate balance between competing molecular and supramolecular CT effects, thereby creating a non-centrosymmetric and thus SHG-active material; secondly, its consequentially favourable packing arrangement and supramolecular CT effects contribute significantly to the magnitude of the SHG effect, despite the non-optimal phase-matching angle of the material. The hydrogen bonds concerned may be classified as weak, but nevertheless are evidently highly influential, especially since they appear to form at the expense of any classical  $\text{O}-\text{H}\cdots\text{X}$  or  $\text{N}-\text{H}\cdots\text{X}$  hydrogen bonds, despite the presence of such strong hydrogen-bond donors.

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