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# 2-Amino derivatives of 5-nitrophenylacetamide

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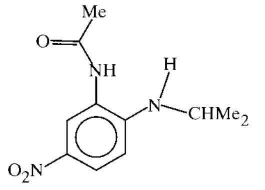
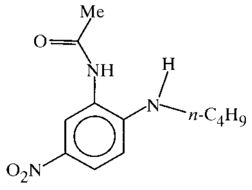
The structures of the potential non-linear optical (NLO) materials *N*-[2-(isopropylamino)-5-nitrophenyl]acetamide, (I) $C_{11}H_{15}N_3O_3$, and *N*-[2-(butylamino)-5-nitrophenyl]acetamide, (II) $C_{12}H_{17}N_3O_3$, have been investigated by X-ray analysis. To compare them with the structure of *N*-[2-(dimethylamino)-5-nitrophenyl]acetamide, (III) $C_{10}H_{13}N_3O_3$, a known NLO compound, we had to redetermine the structure of (III), since it was described only briefly in the literature. There are two molecules in the asymmetric unit of compound (I), which have different orientations of the substituents with respect to the benzene ring. The packing of molecules in (II) and (III) contains stacks but both (I) and (II) crystallize in a centrosymmetric space group, which renders them inappropriate for NLO applications.

## Comment

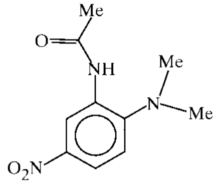
In recent years organic non-linear optical (NLO) materials have been the subject of intensive study because of their crucial advantages in comparison with currently used inorganics (Zyss *et al.*, 1994). To possess NLO properties organic molecules should contain a polar and highly conjugated *p*-electron system terminated with electron donor and acceptor groups. One such compound is the donor–acceptor substituted benzene derivative *N*-[2-(dimethylamino)-5-nitrophenyl]-acetamide, (III), which crystallizes in a non-centrosymmetric space group and which therefore allows second-harmonic generation (Baumert *et al.*, 1987; Norman *et al.*, 1987). As a part of a search for new NLO materials (Antipin *et al.*, 1997, 1998), we synthesized two new compounds, *N*-[2-(isopropylamino)-5-nitrophenyl]acetamide, (I), and *N*-[2-(butylamino)-5-nitrophenyl]acetamide, (II), which are analogous to (III). In this work we present the results of structural investigations of the compounds (I), (II) and (III). Despite the fact that the structure of (III) has been published at least twice, it was discussed only very briefly in each case (Baumert *et al.*, 1987; Norman *et al.*, 1987) and atomic coordinates are absent from these publications and from the Cambridge Structural Database. Thus, to compare the structural peculiarities of (I), (II) and (III) we had to redetermine the crystal structure of (III).



(I)



(II)



(III)

There are two molecules, *A* and *B*, in the asymmetric unit of compound (I) (Fig. 1) which differ primarily by the degree of rotation of the acetamido group with respect to the benzene ring: the C7—N1—C1—C6 torsion angle is −63.7 (3)° in molecule *A* and 38.3 (3)° in molecule *B*. In addition, the aminoisopropyl group of molecule *A* is twisted with respect to the ring somewhat more than that of molecule *B* [the C9—N2—C2—C3 torsion angles are −11.9 (3) and −3.9 (3)°, respectively]. Molecules of (II) (Fig. 2) and (III) (Fig. 3) are also non-planar, with respective C7—N1—C1—C6 torsion angles of −57.1 (4) and −46.4 (3)°, and C9—N2—C2—C3 torsion angles of −4.2 (4) and −11.7 (3)°.

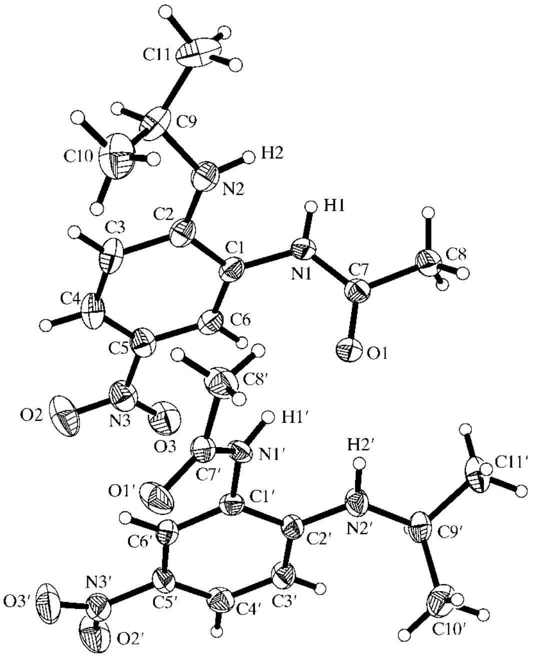


**Figure 1**
A view of the two independent molecules of (I) showing the atom-numbering scheme. Non-H atoms are shown with displacement ellipsoids drawn at the 50% probability level and H atoms are drawn as spheres of arbitrary small radius for clarity.

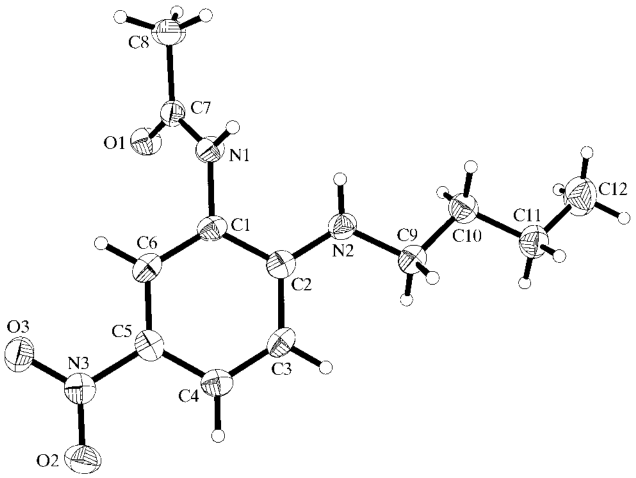


**Figure 2**
A view of a molecule of (II) showing the atom-numbering scheme. Non-H atoms are shown with displacement ellipsoids drawn at the 50% probability level and H atoms are drawn as spheres of arbitrary small radius for clarity.

The nitro groups in molecule *A* of (I) and in (II) and (III) are nearly coplanar with the benzene ring, with the O2—N3—C5—C4 torsion angle adopting values of −3.8 (3), −0.2 (4) and −0.5 (3)°, but in molecule *B* of (I) this group is rotated out of the ring plane by −15.7 (3)°. All bond lengths in the molecules studied are close to standard values (Allen *et al.*, 1987).

In the crystal phase molecules (II) and (III) are stacked along the [100] direction, linked by intermolecular N—H···O bonds (Tables 2 and 3) forming infinite chains. In addition, in (II) neighbouring stacks (symmetry code: $-x$, $-y$, $-z$) are connected by bifurcated intermolecular hydrogen bonds involving O3 (Table 2). In the case of (I), infinite zigzag chains due to intermolecular N—H···O bonds (Table 1) are observed, and molecules *A* and *B* alternate within them. Stacking is absent here. Finally, X-ray investigation has shown that (I) and (II) crystallize in centrosymmetric space groups, where the second-order NLO effect is necessarily absent, rendering these compounds inappropriate as possible NLO materials.

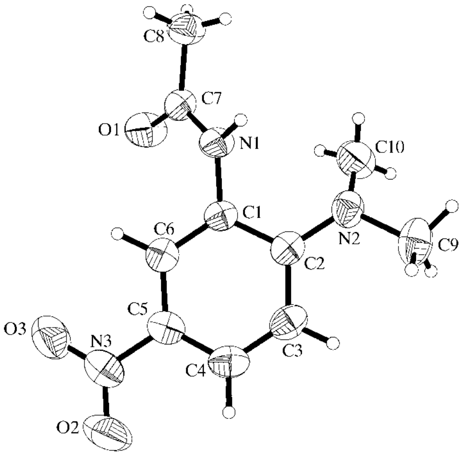


**Figure 3**
A view of a molecule of (III) showing the atom-numbering scheme. Non-H atoms are shown with displacement ellipsoids drawn at the 50% probability level and H atoms are drawn as spheres of arbitrary small radius for clarity.

## Experimental

Compounds (I), (II) and (III) were prepared according to a known procedure (Martinez *et al.*, 1993). Suitable single crystals were obtained by isothermal evaporation of solvent from solutions of (I), (II) and (III) in ethanol at ambient temperature.

### Compound (I)

*Crystal data*

$C_{11}H_{15}N_3O_3$
$M_r$ = 237.26
Monoclinic, $P2_1/n$
$a$ = 13.408 (7) Å
$b$ = 13.277 (4) Å
$c$ = 13.577 (6) Å
$\beta$ = 103.07 (4)°
$V$ = 2354.3 (18) Å$^3$
$Z$ = 8

$D_x$ = 1.339 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta$ = 10–11°
$\mu$ = 0.099 mm$^{-1}$
$T$ = 293 (2) K
Prism, yellow
0.4 × 0.3 × 0.3 mm

*Data collection*

Syntex $P2_1/PC$ diffractometer
$\theta/2\theta$ scans
4351 measured reflections
4164 independent reflections
2976 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.039
$\theta_{\rm max}$ = 25.05°

$h = -12 \rightarrow 15$
$k = -7 \rightarrow 15$
$l = -16 \rightarrow 15$
2 standard reflections every 98 reflections
intensity decay: 4.7%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.110
$S$ = 1.073
4106 reflections
427 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0622P)^2 + 1.0315P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ = 0.001
$\Delta\rho_{\rm max}$ = 0.20 e Å$^{-3}$
$\Delta\rho_{\rm min}$ = −0.27 e Å$^{-3}$

**Table 1**
Hydrogen-bonding geometry (Å, °) for (I).

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1···O1′$^{\rm i}$ | 0.86 (2) | 1.99 (3) | 2.806 (3) | 159 (2) |
| N2—H2···O1′$^{\rm i}$ | 0.92 (3) | 2.25 (3) | 3.054 (3) | 147 (2) |
| N1′—H1′···O1 | 0.85 (2) | 2.00 (2) | 2.834 (3) | 168 (2) |
| N2′—H2′···O1 | 0.85 (3) | 2.19 (3) | 3.014 (3) | 162 (2) |

Symmetry code: (i) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$.

### Compound (II)

*Crystal data*

$C_{12}H_{17}N_3O_3$
$M_r$ = 251.29
Triclinic, $P\overline{1}$
$a$ = 4.874 (2) Å
$b$ = 11.002 (5) Å
$c$ = 12.335 (7) Å
$\alpha$ = 76.14°
$\beta$ = 82.27°
$\gamma$ = 86.99°
$V$ = 636.2 (5) Å$^3$

$Z$ = 2
$D_x$ = 1.312 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta$ = 10–11°
$\mu$ = 0.096 mm$^{-1}$
$T$ = 193 (2) K
Prism, yellow
0.5 × 0.4 × 0.3 mm

*Data collection*

Syntex $P2_1/PC$ diffractometer
$\theta/2\theta$ scans
2900 measured reflections
2569 independent reflections
1391 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.060$
$\theta_{\rm max} = 27.06°$

$h = -5 \rightarrow 5$
$k = -14 \rightarrow 14$
$l = -15 \rightarrow 15$
2 standard reflections
every 98 reflections
intensity decay: 4.1%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.068$
$wR(F^2) = 0.141$
$S = 1.103$
2503 reflections
173 parameters

H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0901P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.25$ e Å$^{-3}$
$\Delta\rho_{\rm min} = -0.30$ e Å$^{-3}$

**Table 2**
Hydrogen-bonding geometry (Å, °) for (II).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1···O1$^{\rm i}$ | 0.86 (4) | 2.21 (4) | 2.928 (4) | 142 (3) |
| N1—H1···O3$^{\rm ii}$ | 0.86 (4) | 2.55 (4) | 3.247 (4) | 139 (3) |
| N2—H2···O1$^{\rm i}$ | 0.87 (3) | 2.21 (4) | 2.973 (4) | 146 (3) |

Symmetry codes: (i) $x - 1, y, z$; (ii) $-x, 1 - y, 1 - z$.

## Compound (III)

*Crystal data*

$C_{10}H_{13}N_3O_3$
$M_r = 223.23$
Monoclinic, $P2_1$
$a = 4.7860$ (10) Å
$b = 13.030$ (3) Å
$c = 8.727$ (2) Å
$\beta = 94.38$ (3)°
$V = 542.6$ (2) Å$^3$
$Z = 2$

$D_x = 1.366$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 24
reflections
$\theta = 10$–$11°$
$\mu = 0.103$ mm$^{-1}$
$T = 293$ (2) K
Needle, yellow
0.4 × 0.1 × 0.1 mm

*Data collection*

Siemens $P3$ diffractometer
$\theta/2\theta$ scans
2053 measured reflections
1817 independent reflections
1486 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.033$
$\theta_{\rm max} = 25.07°$

$h = 0 \rightarrow 5$
$k = -15 \rightarrow 15$
$l = -10 \rightarrow 10$
2 standard reflections
every 98 reflections
intensity decay: 4.8%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.085$
$S = 1.061$
1754 reflections
193 parameters
H-atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0645P)^2$
$+ 0.0191P]$ where
$P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.012$
$\Delta\rho_{\rm max} = 0.11$ e Å$^{-3}$
$\Delta\rho_{\rm min} = -0.12$ e Å$^{-3}$

**Table 3**
Hydrogen-bonding geometry (Å, °) for (III).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1···O1$^{\rm i}$ | 0.86 | 2.04 | 2.875 (2) | 163 |

Symmetry code: (i) $1 + x, y, z$.

For (II), H atoms on N were located in difference Fourier syntheses and then refined freely, those in methyl groups were located similarly and refined as part of rigid rotating groups, and all others were placed geometrically. In (III), the Hl(—Nl) atom was treated as a riding atom; all other H atom positions were refined isotropically.

For all compounds, data collection: *P*3 (Siemens, 1989); cell refinement: *P*3; data reduction: *XDISK* (Siemens, 1991); program(s) used to solve structure: *SHELXTL*/*PC* (Sheldrick, 1994); program(s) used to refine structure: *SHELXTL*/*PC*; molecular graphics: *SHELXTL*/*PC*; software used to prepare material for publication: *SHELXTL*/*PC*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1387). Services for accessing these data are described at the back of the journal.

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