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1,3-Bis(ethylamino)-2-nitrobenzene, 1,3-bis(*n*-octylamino)-2-nitrobenzene and 4-ethylamino-2-methyl-1*H*-benzimidazole

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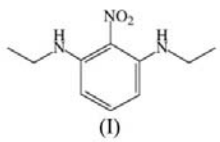
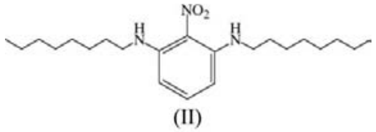
1,3-Bis(ethylamino)-2-nitrobenzene, $C_{10}H_{15}N_3O_2$, (I), and 1,3-bis(*n*-octylamino)-2-nitrobenzene, $C_{22}H_{39}N_3O_2$, (II), are the first structurally characterized 1,3-bis(*n*-alkylamino)-2-nitrobenzenes. Both molecules are bisected though the nitro N atom and the 2-C and 5-C atoms of the ring by twofold rotation axes. Both display intramolecular N—H···O hydrogen bonds between the amine and nitro groups, but no intermolecular hydrogen bonding. The nearly planar molecules pack into flat layers *ca* 3.4 Å apart that interact by hydrophobic interactions involving the *n*-alkyl groups rather than by π–π interactions between the rings. The intra- and intermolecular interactions in these molecules are of interest in understanding the physical properties of polymers made from them. Upon heating in the presence of anhydrous potassium carbonate in dimethylacetamide, (I) and (II) cyclize with formal loss of hydrogen peroxide to form substituted benzimidazoles. Thus, 4-ethylamino-2-methyl-1*H*-benzimidazole, $C_{10}H_{13}N_3$, (III), was obtained from (I) under these reaction conditions. Compound (III) contains two independent molecules with no imposed internal symmetry. The molecules are linked into chains *via* N—H···N hydrogen bonds involving the imidazole rings, while the ethylamino groups do not participate in any hydrogen bonding. This is the first reported structure of a benzimidazole derivative with 4-amino and 2-alkyl substituents.

Comment

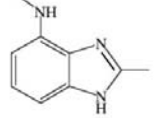
This report is part of our continuing work on polyamines. In our earlier studies (Teng *et al.*, 2006), polyamines were synthesized by the reactions of homologous aliphatic diamines with 1,5-difluoro-2,4-dinitrobenzene. These polymers are only soluble in concentrated mineral acids, including sulfuric, nitric and perchloric acids, at room temperature. This excellent solvent resistance is believed to be due to the existence of strong inter- and intrachain hydrogen-bonding interactions, which arise from the presence of secondary amine groups *ortho* to an aryl nitro group in the polymer repeat unit. As an extension of this study, we have prepared two more series of polyamines by the reactions of homologous aliphatic diamines with 2,6-difluoronitrobenzene and 2,4-difluoronitrobenzene, details of which will be published elsewhere. As a precursor to the polymer syntheses, model compounds were synthesized from aliphatic diamines and the isomeric difluorides mentioned above. We report herein the detailed structural characterization of the secondary diamines 1,3-bis(ethylamino)-2-nitrobenzene, (I), and 1,3-bis(*n*-octylamino)-2-nitrobenzene, (II), derived from 2,6-difluoronitrobenzene. These compounds were synthesized successfully at a reaction temperature of 393 K in dimethylacetamide (DMAC), in the presence of excess anhydrous potassium carbonate and toluene. These reactions failed to yield the desired compounds when the reaction temperature exceeded 403 K. In order to understand this, the reaction mixture was analyzed periodically by gas chromatography and mass spectroscopy (GC/MS) with increasing reaction temperatures. These studies suggest that the desired diamines, which form quantitatively at or below 403 K, undergo further transformations as the temperature is gradually increased. 4-Ethylamino-2-methyl-1*H*-benzimidazole, (III), was obtained from (I) during this process. Benzimidazole derivative (III) is the only product that could be unequivocally identified by GC/MS analyses. However, the presence of a number of other organic products, probably oligomeric in nature, was evident during the purification of (III) using column chromatography. Compound (II) underwent a similar reaction to yield 2-heptyl-4-(*n*-octylamino)-1*H*-benzimidazole. However, in spite of repeated attempts, we were unable to obtain crystals of appropriate quality.



(I)



(II)



(III)

Molecules of (I) are bisected by a twofold rotation axis that contains atoms N1, C1, C4 and H4 (Fig. 1). The H atoms on the N atoms of the ethylamino groups participate in strong intramolecular hydrogen bonds with the O atoms of the adjacent nitro group (Table 1). This pattern has been observed previously in molecules with primary amine groups on both sides of a nitro group (Ammon *et al.*, 1982). A search of the

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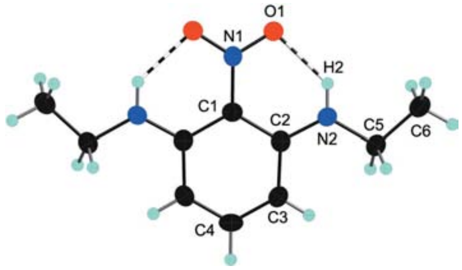

Figure 1
The molecular structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate hydrogen bonds. The asymmetric unit consists of one-half of the molecule and unlabeled atoms are related to labeled atoms by the symmetry operator $(-x + \frac{3}{2}, y, -z + \frac{3}{2})$.

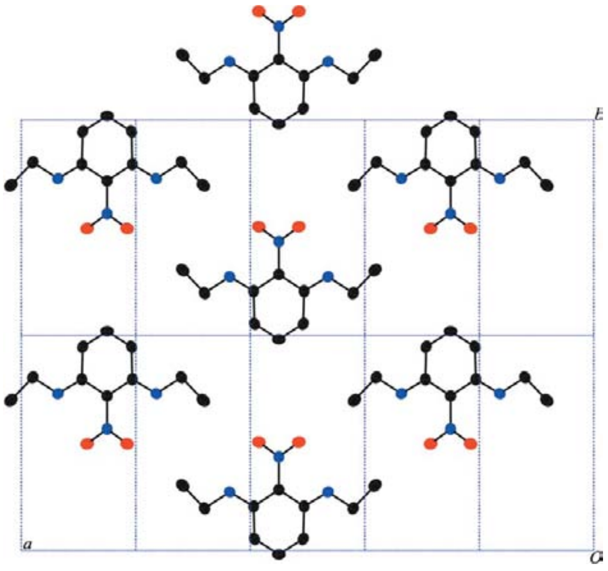

Figure 2
A single layer of molecules of (I), viewed along the *c* axis. Note the absence of intermolecular N—H···O hydrogen bonding.

Cambridge Structural Database (CSD, Version 5.29 plus update of January 2008; Allen, 2002) revealed no prior reports of 1,3-bis(*n*-alkylamino)-2-nitrobenzene structures, so this would appear to be the first example involving secondary amines. The ethyl groups adopt an *anti* conformation (C2—N2—C5—C6 torsion angle *ca* 180°), with the result that the molecules are essentially planar. The molecules pack into flat layers parallel to $(10\overline{3})$ (Fig. 2). It should be noted that there are no intermolecular hydrogen bonds involving the amine H atoms. The packing is thus dominated by hydrophobic interactions. Interestingly, although the interlayer spacing (*ca* 3.4 Å) is short enough for strong π–π interactions, the layers are actually shifted so that the rings are not over one another.

Molecules of (II) are very similar to those of (I), being also bisected through the nitro group and ring by a twofold axis (Fig. 3) and displaying the same intramolecular N—H···O hydrogen bonding (Table 2). The *n*-octyl groups are in the

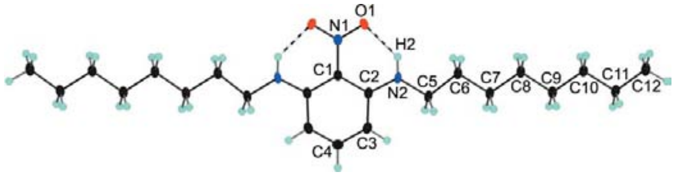

Figure 3
The molecular structure of (II), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate hydrogen bonds. The asymmetric unit consists of one-half of the molecule and unlabeled atoms are related to labeled atoms by the symmetry operator $(-x, y, -z + \frac{1}{2})$.

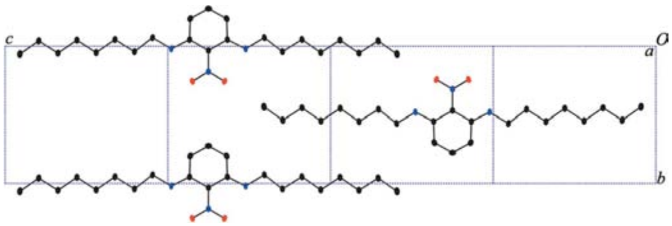

Figure 4
A single layer of molecules of (II), viewed along the *a* axis. Note the absence of intermolecular N—H···O hydrogen bonding.

zigzag *anti* conformation and the essentially planar molecules pack in flat layers parallel to $(30\overline{1})$ with no intermolecular N—H···O hydrogen bonding (Fig. 4). Similar to (I), the layers are separated by about 3.4 Å, but the rings are not face-to-face. Rather, the dominant interaction is between the hydrophobic octyl chains. This preference for interactions between long alkyl chains over those between phenyl rings has also been noted in *N*-(*n*-decyl)-4-nitroaniline (Yonkey *et al.*, 2008). The absence of intermolecular hydrogen bonding between the amine and nitro groups in the monomers, though understandable given the strong intramolecular interactions, does raise questions about what may be taking place in the polymers. We do note, however, that there are examples of aryl nitro compounds with *ortho* secondary amines in which the amine participates in simultaneous intra- and intermolecular N—H···O hydrogen bonds (Panunto *et al.*, 1987).

Compound (III) is formed from (I) by an internal cyclization in which a new bond is formed between the α-C atom of one of the ethyl groups and the nitro N atom. In the process, the two α-H atoms and both nitro O atoms are lost. The presence of a peak of 34 a.m.u. in the mass spectrum suggests the possibility of hydrogen peroxide as the decomposition product. Structurally, (III) occurs as two independent molecules that occupy general positions and do not differ significantly in conformation (Fig. 5). The molecules are essentially planar, with a dihedral angle of 57.25 (1)° between them. In both molecules, the amine N atom is most displaced from the least-squares plane of the non-H atoms, *viz.* by 0.124 (1) Å for atom N12 and by 0.057 (1) Å for atom N22. Similar to what is found in benzimidazole itself (Vijayan *et al.*, 2006), the molecules in (III) are linked by N—H···N hydrogen bonds between the protonated and unprotonated N atoms of the imidazole rings of adjacent molecules into chains running

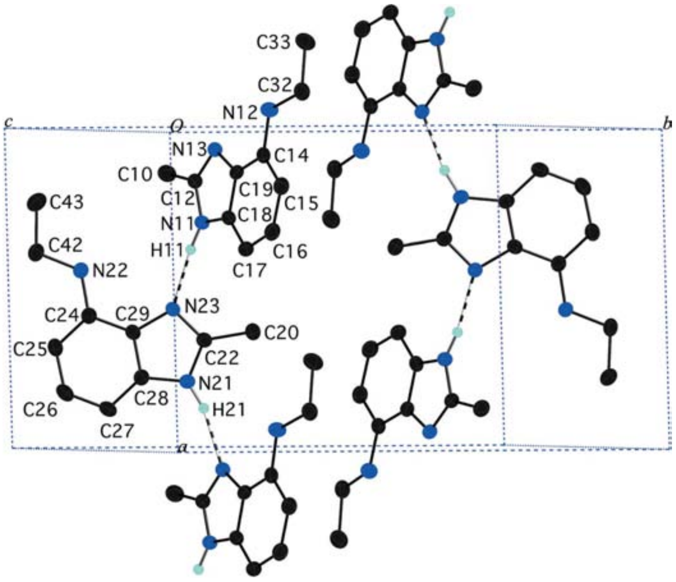

Figure 5
A packing diagram for (III), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The asymmetric unit consists of two independent molecules. N—H···N hydrogen bonds (dashed lines) involving the imidazole rings link the molecules into chains running parallel to the *a* axis. There are no hydrogen bonds involving the amine N atoms.

parallel to the *a* axis. The amine groups do not participate in any N—H···N hydrogen bonds. Benzimidazole crystallizes in a noncentrosymmetric space group and is of interest as a potential nonlinear optical material (Vijayan *et al.*, 2006). However, in spite of the similar hydrogen bonding, (III) crystallizes in a centrosymmetric space group. The presence of intermolecular hydrogen bonds in (III) is reflected in the significantly higher melting point compared with (I) and (II). A search of the CSD found no benzimidazole derivatives with alkyl groups in the 4-position and an *R* group in the 2-position, making this the first structurally characterized example.

Experimental

Compounds (I) and (II) were prepared by similar routes. Anhydrous potassium carbonate (1.0943 g, 0.008 mol) and a solution of ethylamine (1.0805 g, 0.0240 mol; 70% in water) or octylamine (0.7284 g, 0.006 mol) in dimethylacetamide (DMAC, 8 ml) were combined in a 100 ml three-necked round-bottomed flask fitted with a nitrogen inlet, a thermometer, a magnetic stirring bar and a Dean–Stark trap with a condenser. To the stirred solution was added 2,6-difluoronitrobenzene (0.4342 g, 0.0027 mol) in DMAC (5 ml) was added. Additional DMAC (8 ml) was used to wash the transfer container and this was added to the reaction mixture, followed by the addition of toluene (20 ml). The color of the reaction mixture turned bright red when the temperature reached 343 K. The temperature of the reaction mixture was raised to 393 K, and the reaction was allowed to continue at this temperature for 3 h. Water, the by-product of the reaction, was removed *via* azeotropic distillation with toluene. On completion of the reaction, the reaction mixture was allowed to cool to room temperature and diluted with dichloromethane (30 ml). The resulting heterogeneous mixture was filtered through Celite at reduced pressure, and the solvents from the dark-red filtrate were removed under high vacuum to yield a bright-red solid residue. The crude product was dissolved in hexane (15 ml), transferred to a separating funnel and washed repeatedly with deionized water. The organic layer was collected, dried over anhydrous magnesium sulfate and filtered, and the filtrate was evaporated using a rotary evaporator to yield a bright-red solid. Crystals suitable for X-ray diffraction were obtained by recrystallization from hexane. Analysis for compound (I): yield 65%; m.p. 336–338 K; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.6 (*s*, 2H), 7.1 (*m*, 1H), 5.9 (*d*, 2H), 3.2 (*m*, 3H), 1.3 (*t*, 6H); ^{13}C NMR (CDCl$_3$): δ 148.51, 137.06, 121.01, 98.01, 38.34, 14.42; IR (KBr, $\nu >$ 1400 cm^{-1}): 3347, 2980, 2860, 1582, 1515, 1472; MS (*m*/*z*) (% base peak): 209 (85), 174 (100), 132 (72.5), 147 (55). Analysis for compound (II): yield 70%; m.p. 343–345 K; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.7 (*t*, 2H), 7.1 (*t*, 1H), 5.8 (*d*, 2H), 3.2 (*m*, 4H), 1.7 (*m*, 4H), 1.3 (*m*, 20H), 0.9 (*t*, 6H); ^{13}C NMR (CDCl$_3$): δ 148.69, 136.99, 97.88, 43.76, 32.02, 29.51, 29.42, 28.99, 27.40, 22.86, 14.31; IR (KBr, $\nu >$ 1400 cm^{-1}): 3343, 2957, 2926, 2850, 1583, 1515, 1471; MS (*m*/*z*) (% base peak): 377 (63.2), 342 (97.7), 244 (40.3), 232 (43.7), 134 (100). Compound (III) was synthesized from (I) (prepared as described above) by taking the red solution obtained after azeoptropic removal of water and heating it to 433 K for 24 h. During this time, the color gradually turned dark brown. The reaction solution was then diluted with dichloromethane (30 ml). The resulting heterogeneous mixture was filtered through Celite at reduced pressure and solvents were removed under high vacuum. The crude product was dissolved in dichloromethane (15 ml), transferred to a separating funnel and washed repeatedly with deionized water. The organic layer was collected, dried over anhydrous magnesium sulfate and filtered, and the filtrate was evaporated using a rotary evaporator to yield a dark-brown solid. The crude product was eluted on a neutral alumina column using dichloromethane–ethyl acetate (70:30 *v*/*v*) to obtain the desired compound, *viz.* (III). The blue–green solid was recrystallized from hexane. Analysis for compound (III): yield: 15%; m.p. 432–434 K; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.1 (*m*, 1H), 6.7 (*m*, 1H), 6.3 (*m*, 1H), 3.3 (*q*, 2H), 2.6 (*s*, 3H), 1.3 (*t*, 3H); ^{13}C NMR (CDCl$_3$): δ 148.24, 139.90, 134.53, 131.55, 124.02, 101.55, 99.67, 38.39, 30.00, 15.06; IR (KBr, $\nu >$ 1400 cm^{-1}): 3366, 2961, 1607, 1540, 1422; MS (*m*/*z*) (% base peak): 175 (38), 132 (38), 160 (100).

Compound (I)

Crystal data

$C_{10}H_{15}N_3O_2$
M_r = 209.25
Monoclinic, $P2/n$
a = 5.0425 (6) Å
b = 9.2564 (10) Å
c = 11.4901 (13) Å
β = 102.492 (2)°

V = 523.61 (10) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 140 (2) K
0.40 × 0.06 × 0.03 mm

Data collection

Bruker SMART 6000 CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min}$ = 0.77, $T_{\max}$ = 1.00 (expected range = 0.768–0.997)

3016 measured reflections
1017 independent reflections
919 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.055

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.121
S = 1.15
1017 reflections

100 parameters
All H-atom parameters refined
$\Delta\rho_{\max}$ = 0.31 e Å^{-3}
$\Delta\rho_{\min}$ = −0.16 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O1	0.85 (2)	1.91 (2)	2.566 (1)	133 (2)

Compound (II)

Crystal data

$C_{22}H_{39}N_3O_2$
M_r = 377.56
Monoclinic, $C2/c$
a = 21.5603 (16) Å
b = 9.1066 (7) Å
c = 12.6778 (10) Å
β = 121.560 (2)°
V = 2121.0 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 140 (1) K
0.38 × 0.19 × 0.03 mm

Data collection

Bruker SMART 6000 CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min}$ = 0.841, $T_{\max}$ = 1.000 (expected range = 0.839–0.998)
8645 measured reflections
2568 independent reflections
2012 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.149
S = 1.06
2568 reflections
202 parameters
All H-atom parameters refined
$\Delta\rho_{\max}$ = 0.43 e Å^{-3}
$\Delta\rho_{\min}$ = −0.28 e Å^{-3}

Compound (III)

Crystal data

$C_{10}H_{13}N_3$
M_r = 175.23
Monoclinic, $P2_1/n$
a = 9.6166 (3) Å
b = 16.2072 (5) Å
c = 12.1236 (3) Å
β = 93.278 (1)°
V = 1886.47 (10) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 140 (2) K
0.36 × 0.30 × 0.30 mm

Data collection

Bruker SMART 6000 CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min}$ = 0.893, $T_{\max}$ = 1.000 (expected range = 0.873–0.977)
19605 measured reflections
4120 independent reflections
3759 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.019

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.118
S = 1.09
4120 reflections
339 parameters
All H-atom parameters refined
$\Delta\rho_{\max}$ = 0.30 e Å^{-3}
$\Delta\rho_{\min}$ = −0.24 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O1	0.844 (18)	1.910 (18)	2.570 (1)	134 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
N11—H11···N23	0.945 (17)	1.896 (18)	2.8293 (14)	169.2 (15)
N21—H21···N13$^{\rm i}$	0.950 (17)	1.946 (17)	2.8761 (15)	165.9 (15)

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

All H atoms were located in difference Fourier syntheses and were refined isotropically [C—H = 0.915 (17)–1.030 (14) Å].

For all compounds, data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Version 6.10; Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *CrystalMaker* (Palmer, 2006); software used to prepare material for publication: *SHELXTL* and local programs.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3210). Services for accessing these data are described at the back of the journal.

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