

***N,N'*-Diethyl-4-nitrobenzene-1,3-diamine, 2,6-bis(ethylamino)-3-nitrobenzonitrile and bis(4-ethylamino-3-nitrophenyl) sulfone**Thomas J. Payne,^a Chad R. Thurman,^a Hao Yu,^a Qian Sun,^a Dillip K. Mohanty,^{a*} Philip J. Squattrito,^{a*} Mark-Robin Giolando,^b Christopher R. Brue^b and Kristin Kirschbaum^b^aDepartment of Chemistry, Central Michigan University, Mount Pleasant, MI 48859, USA, and ^bDepartment of Chemistry, University of Toledo, Toledo, OH 43606, USA
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Received 11 June 2010

Accepted 15 June 2010

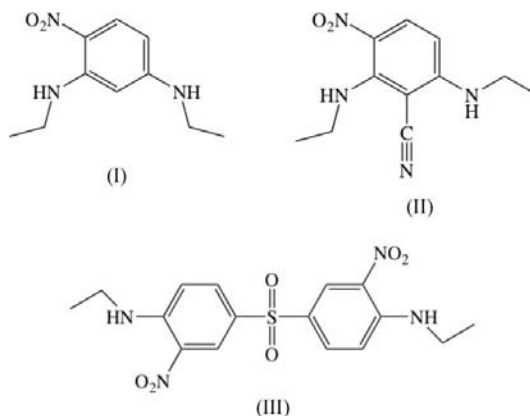
Online 23 June 2010

N,N'-Diethyl-4-nitrobenzene-1,3-diamine, C₁₀H₁₅N₃O₂, (I), crystallizes with two independent molecules in the asymmetric unit, both of which are nearly planar. The molecules differ in the conformation of the ethylamine group *trans* to the nitro group. Both molecules contain intramolecular N—H···O hydrogen bonds between the adjacent amine and nitro groups and are linked into one-dimensional chains by intermolecular N—H···O hydrogen bonds. The chains are organized in layers parallel to (101) with separations of *ca* 3.4 Å between adjacent sheets. The packing is quite different from what was observed in isomeric 1,3-bis(ethylamino)-2-nitrobenzene. 2,6-Bis(ethylamino)-3-nitrobenzonitrile, C₁₁H₁₄N₄O₂, (II), differs from (I) only in the presence of the nitrile functionality between the two ethylamine groups. Compound (II) crystallizes with one unique molecule in the asymmetric unit. In contrast with (I), one of the ethylamine groups, which is disordered over two sites with occupancies of 0.75 and 0.25, is positioned so that the methyl group is directed out of the plane of the ring by approximately 85°. This ethylamine group forms an intramolecular N—H···O hydrogen bond with the adjacent nitro group. The packing in (II) is very different from that in (I). Molecules of (II) are linked by both intermolecular amine–nitro N—H···O and amine–nitrile N—H···N hydrogen bonds into a two-dimensional network in the (10 $\bar{2}$) plane. Alternating molecules are approximately orthogonal to one another, indicating that π – π interactions are not a significant factor in the packing. Bis(4-ethylamino-3-nitrophenyl) sulfone, C₁₆H₁₈N₄O₆S, (III), contains the same *ortho* nitro/ethylamine pairing as in (I), with the position *para* to the nitro group occupied by the sulfone instead of a second ethylamine group. Each 4-ethylamino-3-nitrobenzene moiety is nearly planar and contains the typical intramolecular N—H···O hydrogen bond. Due to the tetrahedral geometry about the S

atom, the molecules of (III) adopt an overall V shape. There are no intermolecular amine–nitro hydrogen bonds. Rather, each amine H atom has a long (H···O *ca* 2.8 Å) interaction with one of the sulfone O atoms. Molecules of (III) are thus linked by amine–sulfone N—H···O hydrogen bonds into zigzag double chains running along [001]. Taken together, these structures demonstrate that small changes in the functionalization of ethylamine–nitroarenes cause significant differences in the intermolecular interactions and packing.

Comment

As part of a continuing investigation of polyamine polymers (Teng *et al.*, 2006; Wang *et al.*, 2009), we have prepared and structurally characterized several series of aromatic nitro compounds with aliphatic amine groups as model compounds for the polymers (Walczak *et al.*, 2008; Teng *et al.*, 2009). Detailed knowledge of the intra- and intermolecular interactions in the model compounds may be useful in interpreting the physical properties (solvent resistance, *etc.*) of polymers containing the same functional groups. In this report, we present the structures of *N,N'*-diethyl-4-nitrobenzene-1,3-diamine, (I), 2,6-bis(ethylamino)-3-nitrobenzonitrile, (II), and bis(4-ethylamino-3-nitrophenyl) sulfone, (III).



Compounds (I) and (II) differ only in the presence of a nitrile group between the ethylamine groups on the latter, while (III) has two nitro- and ethylamine-substituted arene moieties similar to those in (I) joined *via* a sulfone group. In addition, (I) is an isomer of 1,3-bis(ethylamino)-2-nitrobenzene, the structure of which we reported recently (Walczak *et al.*, 2008). Despite the chemical similarities between these compounds, their structures reveal substantial differences in intermolecular interactions and crystal packing.

Compound (I) crystallizes in the monoclinic space group *P*2₁/*c* with two independent molecules in the asymmetric unit (Fig. 1). Both molecules are essentially flat and coplanar [the dihedral angle between the arene planes is 4.56 (7)°], but they differ in terms of the conformation of the ethylamine group *para* to the nitro group. In one molecule, both ethylamine groups are positioned such that the methylene C atoms eclipse atom C2 of the arene ring (*i.e.* the C2—C1—N1—C7 and C2—C3—N2—C9 torsion angles are both close to 0°). In the other

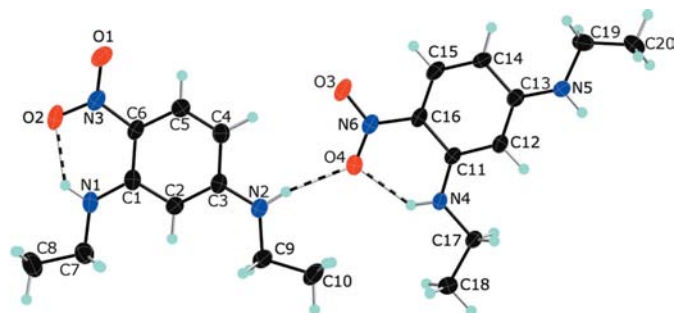


Figure 1

The molecular structure of (I), showing the atom-labelling 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 molecules. Hydrogen bonds are shown as dashed lines.

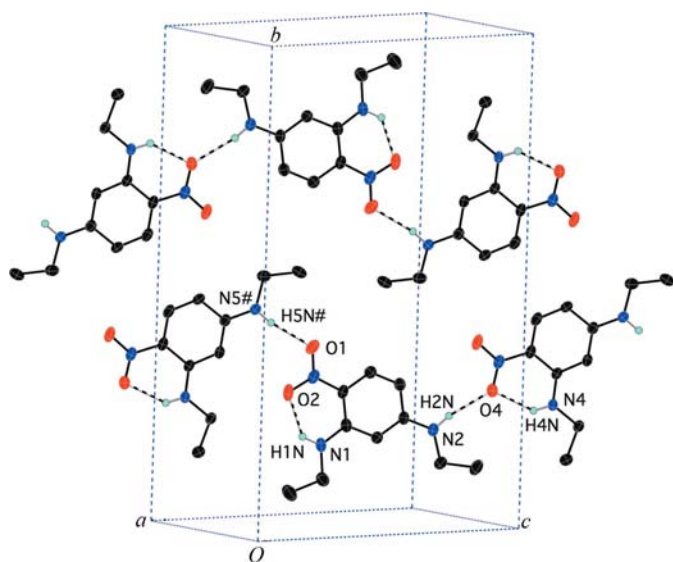


Figure 2

Molecules of (I) linked into chains by N—H...O amine–nitro hydrogen bonds (dashed lines). Portions of two chains are shown and the view is on to the (101) plane. [Symmetry code: (#) $x + 1, y, z - 1$.]

molecule, the ethylamine group *ortho* to the nitro group is oriented similarly, while that *para* to the nitro group is rotated in the opposite direction, such that the C12—C13—N5—C19 torsion angle is 168.42 (16)°. As a result, the latter molecule is slightly less planar than the former.

Both molecules of (I) feature an intramolecular hydrogen bond between the amine H atom and the O atom of the adjacent nitro group (Table 1). This type of interaction is typical for arenes with an amine group *ortho* to a nitro group (Panunto *et al.*, 1987). The two independent molecules are linked by an intermolecular N—H...O hydrogen bond between the amine group on one molecule and the nitro group on the other. Nitro atom O4 thus serves as an acceptor for both intra- and intermolecular hydrogen bonds. Molecules of (I) are linked into one-dimensional chains (Fig. 2) by two amine–nitro hydrogen bonds, *viz.* the N2—H2N...O4 interaction shown in Fig. 1 and an N5—H5N...O1ⁱ interaction [symmetry code: (i) $x - 1, y, z + 1$] (Table 1). Chains are commonly formed by similarly functionalized arenes *via*

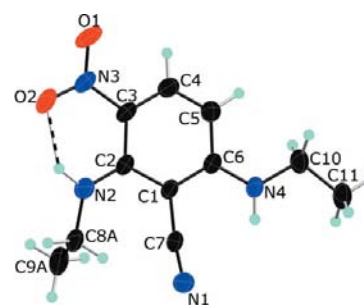


Figure 3

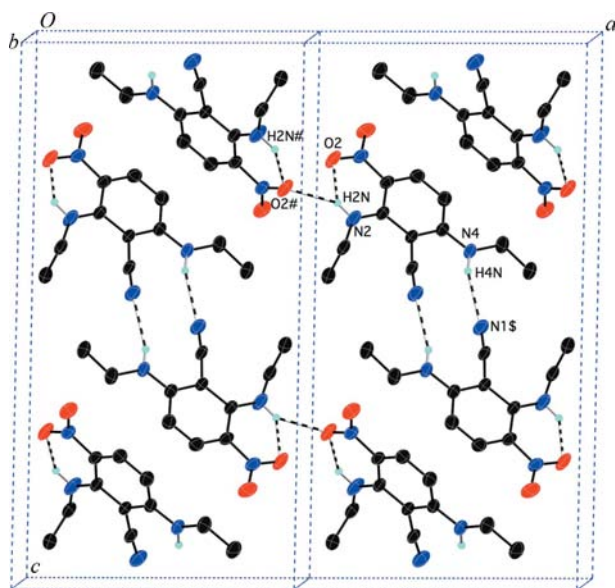
The molecular structure of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The asymmetric unit consists of one molecule. The hydrogen bond is shown as a dashed line.

N—H...O hydrogen bonds (Panunto *et al.*, 1987). The chains in (I) are positioned in the (101) planes of the crystal structure, with the resulting layers separated by *ca* 3.4 Å. The closest rings in adjacent layers are slipped past one another, negating the possibility of significant π – π interactions between molecules in neighbouring sheets.

Previously, we reported the structure of 1,3-bis(ethylamino)-2-nitrobenzene, an isomer of (I) (Walczak *et al.*, 2008). When the nitro group is located between the amine groups, both form intramolecular N—H...O hydrogen bonds and the molecules pack without forming any intermolecular hydrogen bonds. The packing is instead dominated by hydrophobic attractions between the alkyl groups. The difference in intermolecular interactions is reflected in the higher melting point of (I) (381 K) compared with its isomer (336 K).

Compound (II) has the nitro and ethylamine groups arranged as in (I), with an added nitrile functionality between the two ethylamine groups. Compound (II) also crystallizes in $P2_1/c$, but with one independent molecule in the asymmetric unit (Fig. 3). The conformation of the ethylamine group *ortho* to the nitro group is quite different from that in (I). Atoms C8 and C9 are disordered over two positions, *A* and *B*, with occupancies of 0.75 and 0.25, respectively; only the major component is shown in Figs. 3 and 4. The C8A—C9A ethyl group is positioned so that methyl atom C9A is directed out of the plane of the ring at an angle of approximately 85° [C2—N2—C8A—C9A torsion angle $-85.4(2)^\circ$], whereas the rest of the molecule is nearly planar.

As in (I) and all of the amine/nitro-substituted molecules we have examined so far (Walczak *et al.*, 2008; Teng *et al.*, 2009), there is an intramolecular hydrogen bond between the adjacent amine and nitro groups of (II) (Table 2). Molecules of (II) are associated *via* two types of intermolecular hydrogen bonds. First, there is a fairly long amine–nitro N2—H2N...O2ⁱ interaction [symmetry code: (i) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$] that connects the molecules into chains along [010] (Fig. 4). Amine atom H2N thus participates in a three-centre hydrogen bond with acceptor atoms O2 (intramolecular) and O2ⁱ (intermolecular). In addition, pairs of molecules are joined by a centrosymmetric pair of hydrogen bonds between the amine group *trans* to the nitro group and the nitrile N atom, *viz.* N4—H4N...N1ⁱⁱ

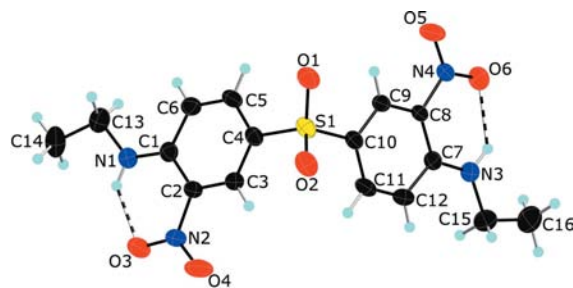
**Figure 4**

Molecules of (II) linked by N—H···O amine–nitro hydrogen bonds (dashed lines) into chains running along [010]. Pairs of molecules are also linked across centres of inversion by N—H···N amine–nitrile hydrogen bonds. Two unit cells are shown and the view is along the *b* axis. [Symmetry codes: (#) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$; (\$) $-x + 1, -y + 1, -z + 1$].

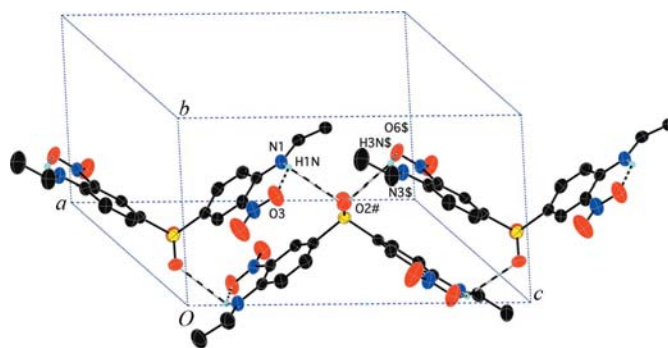
[symmetry code: (ii) $1 - x, 1 - y, 1 - z$] (Table 2). The overall result is a two-dimensional network parallel to the $(10\bar{2})$ plane. Unlike in (I), the molecules of (II) are not all parallel. Rather, alternating molecules are approximately orthogonal to one another [the dihedral angle between the molecules at (x, y, z) and $(-x, y + \frac{1}{2}, -z + \frac{1}{2})$ is $87.53(6)^\circ$], suggesting that π – π interactions are not a significant factor in the packing.

Compound (III) contains the same *ortho* nitro/ethylamine pairing as in (I), with the position *para* to the nitro group occupied by the sulfone instead of a second ethylamine group. It also crystallizes in $P2_1/c$ with one independent molecule in the asymmetric unit (Fig. 5). Each 4-ethylamino-3-nitrobenzene moiety is nearly planar and contains the expected intramolecular N—H···O hydrogen bond. The bond distances and angles around the S atom are within the ranges reported in a recent study of a number of diaryl sulfones, including some with amine and nitro groups on the rings (Rudolph *et al.*, 2009). Due to the tetrahedral geometry around the S atom, the molecules adopt an overall V shape [the dihedral angle between the arene rings is $70.93(4)^\circ$].

There are no intermolecular amine–nitro hydrogen bonds in the structure of (III). Rather, each amine H atom has a long interaction with sulfone atom O2, *viz.* N1—H1N···O2ⁱ [symmetry code: (i) $x, -y + \frac{1}{2}, z + \frac{1}{2}$] and N3—H3N···O2ⁱⁱ [symmetry code: (ii) $x, -y + \frac{1}{2}, z - \frac{1}{2}$] (Table 3). Thus, each amine H atom participates in a three-centre hydrogen bond with two acceptors (an intramolecular nitro O atom and an intermolecular sulfone O atom), while atom O2 serves as an acceptor for both H atoms. A study of N—H···O hydrogen bonds in sulfonates (Pirard *et al.*, 1995) finds a small cluster of three-centre interactions similar to those found in (III) with

**Figure 5**

The molecular structure of (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines.

**Figure 6**

Molecules of (III) linked by N—H···O hydrogen bonds (dashed lines) between the amine H atom and sulfone O atom into double chains running along the [001] direction. A single such chain is shown. [Symmetry codes: (#) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (\$) $x, y, z + 1$].

H···O distances $> 2.6 \text{ \AA}$ and N—H···O angles roughly between 90 and 120° . Molecules of (III) are thus linked through the N—H···O_{sulfone} hydrogen bonds into zigzag double chains running along [001] (Fig. 6). The arene rings of neighbouring molecules in the double chain face each other at a separation of *ca* 3.4 \AA .

Despite the presence of the *ortho* amine and nitro functionalities in all three molecules, the intermolecular hydrogen-bonding patterns and molecular packing are quite different. In particular, one might expect (II) to adopt a similar network of amine–nitro hydrogen bonds to (I), where the H···O distances are around 2.10 \AA . Instead, only one weaker three-centre N—H···O interaction [$\text{H}\cdots\text{O} = 2.47(2) \text{ \AA}$] and a weaker N—H···N amine–nitrile interaction [$\text{H}\cdots\text{N} = 2.361(19) \text{ \AA}$] serve to link the molecules of (II). Inspection of Fig. 2 suggests that the network in (I) would be impossible for (II) because the nitrile N atom would have an unacceptably close contact with a nitro O atom. In the case of (III), the absence of intermolecular N—H···O amine–nitro hydrogen bonds is consistent with previous studies of sulfone molecules containing N—H or O—H bonds, in which it was found that intermolecular N—H···O or O—H···O hydrogen bonds involving the sulfone O atoms are favoured over other interactions (Glidewell *et al.*, 2001; Glidewell & Ferguson, 1996). In particular, in the crystal structure of 4-aminophenyl 4-nitro-

phenyl sulfone (Bertolasi *et al.*, 1993), which contains all of the donor and acceptor groups found in (III), the molecules are linked by amine–sulfone hydrogen bonds only, with no amine–nitro interactions.

Experimental

For the preparation of (I), anhydrous potassium carbonate (5.095 g, 0.036 mol) and a solution of ethylamine (5.714 g, 0.0886 mol; 70% in water) in dimethylacetamide (DMAC, 8 ml) were combined in a 100 ml three-necked round-bottomed flask fitted with a nitrogen inlet, thermometer, magnetic stirring bar, and a Dean–Stark trap fitted with a condenser. To the stirred solution was added 2,4-difluoronitrobenzene (2.349 g, 0.0148 mol) in DMAC (5 ml). Additional DMAC (8 ml) was used to wash the transfer container and this was added to the reaction mixture, followed by toluene (20 ml). The temperature of the reaction mixture was raised to 333 K, held at that temperature for 3 h, then raised to 393 K and the reaction allowed to continue for another 3 h. The colour of the reaction mixture turned bright orange when the temperature reached 393 K. Water, the by-product of the reaction, was removed *via* azeotropic distillation with toluene. On completion of the reaction, the 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–orange filtrate were removed under high vacuum to yield a bright-orange solid residue. The crude product was dissolved in dichloromethane (15 ml), transferred to a separation funnel and washed repeatedly with deionized water. The organic layer was collected, dried over magnesium sulfate, filtered, and the filtrate evaporated using a rotary evaporator to yield a bright-orange solid. Crystals of (I) suitable for X-ray diffraction were obtained by recrystallization from an ethanol–dichloromethane solution (3:1 *v/v*) (yield 73.4%; m.p. 381–382 K). Spectroscopic analysis for (I): $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 8.4 (*t*, 1H), 8.0 (*m*, 1H), 5.9 (*m*, 1H), 5.6 (*m*, 1H), 4.4 (*t*, 1H), 3.3 (*m*, 4H), 1.3 (*t*, 6H); $^{13}\text{C NMR}$ (300 MHz, CDCl_3): δ 200.59, 154.52, 148.70, 129.47, 104.90, 90.10, 38.10, 37.76, 14.61, 14.42; IR (NaCl, $\nu > 1400\text{ cm}^{-1}$): 3340, 3307, 2973, 1623, 1551, 1460, 1397, 1322, 1268, 1197, 1169, 1149; MS (*m/z*) (% base peak): 209 (100), 194 (24.5), 176 (62.8), 160 (44.9), 149 (23.9), 134 (20.2).

Compound (II) was prepared using a similar reaction setup to (I). The flask was charged with anhydrous potassium carbonate (2.246 g, 0.016 mol). Ethylamine (0.573 g, 0.013 mol) was weighed in a one-dram glass vial and dissolved in DMAC (5 ml). The solution was added dropwise to the reaction mixture and the vial was subsequently rinsed with DMAC (5 ml) to ensure complete transfer of the ethylamine. 2,6-Difluoro-3-nitrobenzonitrile (1.197, 0.00650 mol) in DMAC (5 ml) was added, leading to the formation of a cloudy yellow reaction mixture. Additional DMAC (5 ml) was used to wash the transfer container and this was added to the reaction mixture, followed by toluene (20 ml). At approximately 363 K, the colour of the reaction mixture was a cloudy orange. The temperature was raised to 393 K and the reaction allowed to continue at this temperature for 7 h. The crude product was isolated as for (I) and purified by silica-gel chromatography (20% dichloromethane in hexane, *v/v*), to give a bright-yellow solid. Crystals of (II) suitable for X-ray diffraction were obtained by recrystallization from methanol (yield 71%; m.p. 420–422 K). Spectroscopic analysis for (II): $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 9.10 (*t*, 1H), 8.31 (*m*, 1H), 6.00 (*m*, 1H), 5.45 (*t*, 1H), 3.84 (*m*, 2H), 3.36 (*m*, 2H), 1.35 (*m*, 6H); $^{13}\text{C NMR}$ (300 MHz, CDCl_3): δ 157.40, 149.44, 134.17, 124.30, 118.28, 99.67, 77.26, 40.23,

38.49, 15.73, 14.68; IR (NaCl, ν , cm^{-1}): 3330, 3264, 2977, 2201, 1576, 1522, 1496, 1372, 1228, 1163; MS (*m/z*) (% base peak): 234 (67.7), 217 (25), 201 (55.8), 200 (39.6), 199 (28.7), 185 (100), 159 (30.4).

Compound (III) was prepared by a similar procedure from anhydrous potassium carbonate (0.935 g, 0.0075 mol) and a solution of ethylamine (0.489 g, 0.0109 mol; 70% in water) in *N*-methyl-2-pyrrolidone (NMP, 10 ml), to which was added bis(4-fluoro-3-nitrobenzene) sulfone (1.320 g, 0.00383 mol) in NMP (5 ml). Additional NMP (5 ml) was used to wash the transfer container and this was added to the reaction mixture, followed by toluene (20 ml). The bright-yellow and slightly opaque reaction mixture was heated to 333 K, held at that temperature for 30 min and gradually raised to 393 K over a period of 3 h. The bright-yellow product was isolated and purified as for (I). Crystals of (III) suitable for X-ray diffraction were obtained by recrystallization from hexane (yield 69.8%; m.p. 574–576 K). Spectroscopic analysis for (III): $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 8.7 (*s*, 2H), 8.3 (*m*, 2H), 7.9 (*m*, 2H), 6.9 (*m*, 2H), 3.4 (*m*, 4H), 1.4 (*t*, 6H); $^{13}\text{C NMR}$ (300 MHz, CDCl_3): δ 147.66, 133.94, 130.15, 128.04, 128.00, 115.00, 38.31, 14.34; IR (neat, $\nu > 1400\text{ cm}^{-1}$): 3372, 2928, 2860, 1618, 1570, 1522, 1472; MS (*m/z*) (% base peak): 394 (85), 285 (20), 213 (100), 197 (20), 132 (15).

Compound (I)

Crystal data

$\text{C}_{10}\text{H}_{15}\text{N}_3\text{O}_2$	$V = 2172.2 (2) \text{ \AA}^3$
$M_r = 209.25$	$Z = 8$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 7.8148 (5) \text{ \AA}$	$\mu = 0.09 \text{ mm}^{-1}$
$b = 20.9889 (14) \text{ \AA}$	$T = 140 \text{ K}$
$c = 13.2464 (9) \text{ \AA}$	$0.22 \times 0.18 \times 0.04 \text{ mm}$
$\beta = 91.210 (2)^\circ$	

Data collection

Bruker SMART 6000 CCD area-detector diffractometer	23033 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	4717 independent reflections
$T_{\min} = 0.559$, $T_{\max} = 1.000$	3307 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.059$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$	391 parameters
$wR(F^2) = 0.139$	All H-atom parameters refined
$S = 0.97$	$\Delta\rho_{\max} = 0.35 \text{ e \AA}^{-3}$
4717 reflections	$\Delta\rho_{\min} = -0.26 \text{ e \AA}^{-3}$

Compound (II)

Crystal data

$\text{C}_{11}\text{H}_{14}\text{N}_4\text{O}_2$	$V = 1133.9 (17) \text{ \AA}^3$
$M_r = 234.26$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 10.988 (8) \text{ \AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$b = 4.865 (4) \text{ \AA}$	$T = 150 \text{ K}$
$c = 21.220 (18) \text{ \AA}$	$0.55 \times 0.40 \times 0.18 \text{ mm}$
$\beta = 91.62 (4)^\circ$	

Data collection

Bruker SMART 6000 CCD area-detector diffractometer	11551 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	2745 independent reflections
$T_{\min} = 0.819$, $T_{\max} = 1.000$	2346 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.020$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.131$
 $S = 1.04$
 2745 reflections
 228 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.40 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.39 \text{ e } \text{\AA}^{-3}$

Compound (III)

Crystal data

$\text{C}_{16}\text{H}_{18}\text{N}_4\text{O}_6\text{S}$
 $M_r = 394.40$
 Monoclinic, $P2_1/c$
 $a = 15.514 (5) \text{ \AA}$
 $b = 8.573 (4) \text{ \AA}$
 $c = 15.012 (5) \text{ \AA}$
 $\beta = 115.647 (12)^\circ$

$V = 1799.8 (11) \text{ \AA}^3$
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.22 \text{ mm}^{-1}$
 $T = 210 \text{ K}$
 $0.20 \times 0.15 \times 0.09 \text{ mm}$

Data collection

Bruker SMART 6000 CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.793$, $T_{\max} = 1.000$

14699 measured reflections
 3539 independent reflections
 3011 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.030$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.095$
 $S = 1.02$
 3539 reflections

316 parameters
 All H-atom parameters refined
 $\Delta\rho_{\max} = 0.33 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.27 \text{ e } \text{\AA}^{-3}$

The disordered ethyl C atoms in (II) were located in a difference Fourier synthesis. The occupancies of the two sets of atoms, constrained to sum to 1, were initially refined with the U_{iso} values of all four atoms fixed to the same value. At a later stage of the refinement, the occupancies were fixed to the approximate refined values (*i.e.* 0.75 and 0.25) and the atomic displacement parameters were refined. All H atoms were located in difference Fourier syntheses and refined isotropically [$\text{C}-\text{H} = 0.88 (2)-1.05 (4) \text{ \AA}$], except for those of the minor-occupancy ethyl fragment of (II), which were treated as riding, with $\text{C}-\text{H} = 0.99 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ (methylene) or $\text{C}-\text{H} = 0.98 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ (methyl).

For all three compounds, data collection: SMART (Bruker, 2003); cell refinement: SAINT-Plus (Bruker, 2003); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: CrystalMaker (Palmer, 2008); software used to prepare material for publication: SHELXL97.

DKM acknowledges financial support for this project from the Research Excellence Fund of Michigan and a President's Bridge to Commercialization Grant, and sabbatical support from Central Michigan University. The authors thank the College of Arts and Sciences of the University of Toledo and the Ohio Board of Regents for generous financial support of the X-ray diffraction facility.

Table 1

Hydrogen-bond geometry (\AA , $^\circ$) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1N}\cdots\text{O2}$	0.86 (2)	1.950 (19)	2.6091 (18)	132.3 (17)
$\text{N2}-\text{H2N}\cdots\text{O4}$	0.878 (19)	2.12 (2)	2.9835 (18)	167.8 (16)
$\text{N4}-\text{H4N}\cdots\text{O4}$	0.854 (17)	1.961 (17)	2.6330 (16)	134.8 (13)
$\text{N5}-\text{H5N}\cdots\text{O1}^i$	0.881 (18)	2.079 (18)	2.9507 (18)	170.0 (15)

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

Table 2

Hydrogen-bond geometry (\AA , $^\circ$) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N2}-\text{H2N}\cdots\text{O2}$	0.89 (2)	1.88 (2)	2.610 (2)	138.8 (19)
$\text{N2}-\text{H2N}\cdots\text{O2}^i$	0.89 (2)	2.47 (2)	3.123 (2)	130.7 (17)
$\text{N4}-\text{H4N}\cdots\text{N1}^{ii}$	0.873 (18)	2.361 (19)	3.198 (3)	160.7 (15)

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

Table 3

Hydrogen-bond geometry (\AA , $^\circ$) for (III).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1N}\cdots\text{O3}$	0.846 (19)	1.972 (19)	2.646 (2)	135.9 (17)
$\text{N3}-\text{H3N}\cdots\text{O6}$	0.86 (2)	2.00 (2)	2.644 (2)	131.2 (19)
$\text{N1}-\text{H1N}\cdots\text{O2}^i$	0.846 (19)	2.862 (19)	3.332 (2)	117.0 (15)
$\text{N3}-\text{H3N}\cdots\text{O2}^{ii}$	0.86 (2)	2.80 (2)	3.201 (2)	110.4 (17)

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3377). Services for accessing these data are described at the back of the journal.

References

- Bertolasi, V., Ferretti, V., Gilli, P. & Benedetti, P. G. (1993). *J. Chem. Soc. Perkin Trans. 2*, pp. 213–219.
 Bruker (2003). SMART (Version 5.630) and SAINT-Plus (Version 6.45A). Bruker AXS Inc., Madison, Wisconsin, USA.
 Glidewell, C. & Ferguson, G. (1996). *Acta Cryst. C52*, 2528–2530.
 Glidewell, C., Harrison, W. T. A., Low, J. N., Sime, J. G. & Wardell, J. L. (2001). *Acta Cryst. B57*, 190–200.
 Palmer, D. (2008). CrystalMaker. Version 8.1.1. CrystalMaker Software Ltd, Yarnnton, England.
 Panunto, T. W., Urbanczyk-Lipkowska, Z., Johnson, R. & Etter, M. C. (1987). *J. Am. Chem. Soc.* **109**, 7786–7797.
 Pirard, B., Baudoux, G. & Durant, F. (1995). *Acta Cryst. B51*, 103–107.
 Rudolph, F. A. M., Fuller, A. L., Slawin, A. M. Z., Buhl, M., Aitken, R. A. & Woollins, J. D. (2009). *J. Chem. Crystallogr.* **40**, 253–265.
 Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.
 Sheldrick, G. M. (2008). *Acta Cryst. A64*, 112–122.
 Teng, Y. H., Kaminski, G., Zhang, Z., Sharma, A. & Mohanty, D. K. (2006). *Polymer*, **47**, 4004–4011.
 Teng, G., Walczak, C. P., Squatrito, P. J., Mohanty, D. K., Scharer, W., Giolando, M. R. & Kirschbaum, K. (2009). *Acta Cryst. C65*, o76–o80.
 Walczak, C. P., Yonkey, M. M., Squatrito, P. J., Mohanty, D. K. & Kirschbaum, K. (2008). *Acta Cryst. C64*, o248–o251.
 Wang, J., Teng, Y.-H., Hao, Y., Oh-Lee, J. & Mohanty, D. K. (2009). *Polym. J.* **41**, 715–725.