organic compounds

Two new polymorphs of 4-(*N*,*N*-di-methylamino)benzoic acid

Christer B. Aakeröy,* John Desper and Brock Levin

Department of Chemistry, Kansas State University, Manhattan, KS 66506, USA
Correspondence e-mail: aakeroy@ksu.edu

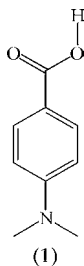Two new polymorphs of 4-(*N*,*N*-dimethylamino)benzoic acid, $C_9H_{11}NO_2$, resulting from the attempted cocrystallization in ethanol of 4-(*N*,*N*-dimethylamino)benzoic acid and a mixture of 3-(*N*,*N*-dimethylamino)benzoic acid and 3-(3-pyridyl)-2-pyridone producing one polymorph, and a mixture of 3-(*N*,*N*-dimethylamino)benzoic acid and 5-methoxy-3,3′-bipyridine producing the second polymorph, have been crystallographically characterized. The primary intermolecular O—H···O hydrogen bonds generate a dimeric acid–acid motif that is present in all three polymorphs.

Comment

It has been demonstrated previously that 4-(*N*,*N*-dimethylamino)benzoic acid, (1), is capable of forming binary (Sharma *et al.*, 1992, 1993) and ternary (Aakeröy *et al.*, 2001) cocrystals as a result of its propensity for engaging in heteromeric complementary hydrogen-bond interactions with carboxylic acids or carboxamides (Aakeröy *et al.*, 2004), as well as with N-heterocyclic compounds, coupled with a capacity to act as a donor moiety in π–π^* charge-transfer donor complexes. With this information in mind, (1) has been used extensively in our laboratory as a cocrystallizing agent, especially since it has also been shown that heterodimers in acid–acid cocrystals (Hanton *et al.*, 1992; Etter, 1990) gain increased stability as a result of the variation in hydrogen-bond donating/accepting ability of the two different carboxylic acid moieties (Etter & Frankenbach, 1989).

(1)

During the course of systematic cocrystallization experiments involving a variety of carboxylic acids [including (1)] and ditopic N-heterocyclic compounds, we obtained two new polymorphs of 4-(*N*,*N*-dimethylamino)benzoic acid. Views of the molecules in forms (II) and (III), with the atom-numbering schemes, are presented in Fig. 1. Polymorph (I) was previously obtained from water–alcohol mixtures (Vyas *et al.*, 1978) and acetone (Anulewicz *et al.*, 1987).

In (II), near-linear O—H···O hydrogen bonds between adjacent crystallographically inequivalent carboxylic acid moieties generate the dominating intermolecular interactions and result in well known dimeric acid–acid motifs [O27—H27···O18^{ii}, with O···O = 2.602 (3) Å, and O17—H17···O28^{i}, with O···O = 2.609 (3) Å; symmetry codes as in Table 1]. Adjacent dimers are positioned with their methyl substituents 'back-to-back', resulting in linear one-dimensional arrangements of dimeric units (Fig. 2).

Form (III) also contains two crystallographically inequivalent molecules; however, symmetry-related molecules form dimers resulting in two distinct chains. The relevant intermolecular O—H···O interactions for the two forms are O17—H17···O18^{i} [O···O = 2.603 (2) Å] and O27—H27···O28^{ii} [O···O = 2.600 (2) Å]. (The H atoms in each of these two interactions are actually disordered between the two O-atom
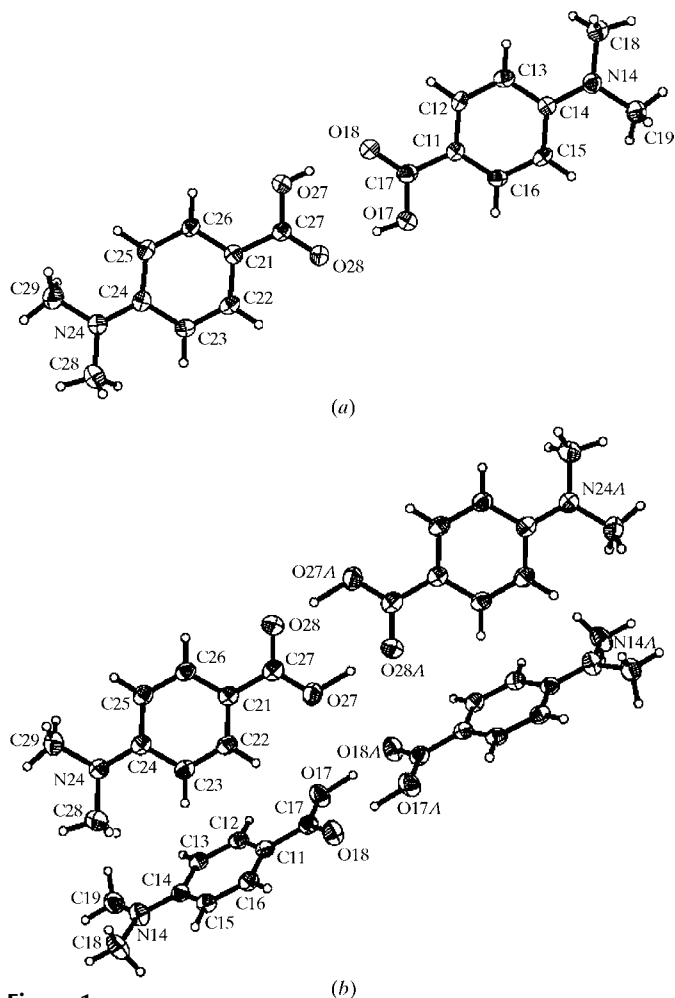

(*a*)

(*b*)

Figure 1
Displacement ellipsoid plots (50% probability level) and atom-numbering schemes for (*a*) form (II) and (*b*) form (III) of 4-(*N*,*N*-dimethylamino)benzoic acid.
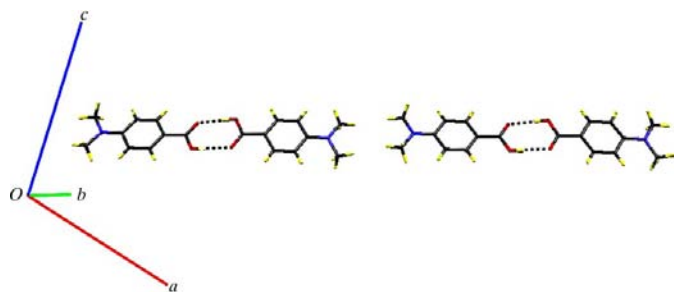
Figure 2
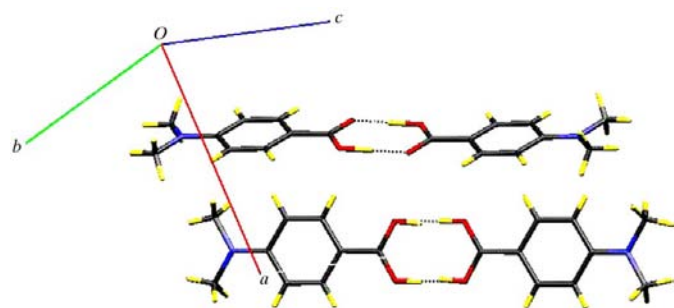A view of adjacent carboxylic dimers in polymorph (II).

Figure 3
A view of the two chains of crystallographically inequivalent dimers in polymorph (III).

sites, so that each O atom acts as a donor and an acceptor with roughly equal populations.) Adjacent dimers organize themselves in the same way as the dimers in forms (I) and (II), with relatively short contacts between methyl groups on adjacent dimers within each chain (Fig. 3).

The amine substituent in all three forms is approximately coplanar with the ring to which it is attached (all relevant torsion angles are less than 5°). It has previously been postulated that polymorphic compounds make good cocrystallizing agents (Aakeröy *et al.*, 2003). This statement is supported by, for example, 3,5-dinitrobenzoic acid, a compound that displays several polymorphic forms (Prince *et al.*, 1991; Kanters *et al.*, 1991; Domenicano *et al.*, 1990) and is known to be an excellent cocrystallizing agent (Pedireddi *et al.*, 1998; Bott *et al.*, 2000; Grabowski *et al.*, 2001). In light of the new polymorphs of (1), the behaviour of 4-(N,N-dimethylamino)benzoic acid lends further support to the notion that good cocrystallizing agents with appropriate hydrogen-bonding substituents are quite likely to be found amongst polymorphic compounds.

Experimental

Crystals of polymorphs (II) and (III) were obtained by slow evaporation of 50% aqueous ethanol solutions of 4-(N,N-dimethylamino)benzoic acid, 3-(N,N-dimethylamino)benzoic acid and 3-(3-pyridyl)-2-pyridone (in a 1:1:1 stoichiometry), and of 4-(N,N-dimethylamino)benzoic acid, 3-(N,N-dimethylamino)benzoic acid and 5-methoxy-3,3′-bipyridine (in a 1:1:1 stoichiometry), respectively.

Polymorph (II)

Crystal data

$C_9H_{11}NO_2$	$D_x = 1.320$ Mg m^{-3}
$M_r = 165.19$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 1626
$a = 10.3202$ (10) Å	reflections
$b = 7.4068$ (8) Å	$\theta = 2.8$–27.7°
$c = 11.2845$ (11) Å	$\mu = 0.09$ mm^{-1}
$\beta = 105.505$ (5)°	$T = 173$ (2) K
$V = 831.19$ (15) Å^3	Plate, colorless
$Z = 4$	$0.35 \times 0.30 \times 0.10$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	$R_{int} = 0.054$
	$\theta_{max} = 28.0°$
φ and ω scans	$h = -13 \rightarrow 12$
5542 measured reflections	$k = -9 \rightarrow 9$
1982 independent reflections	$l = -14 \rightarrow 14$
1280 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.047$	
$wR(F^2) = 0.132$	
$S = 0.96$	$w = 1/[\sigma^2(F_o^2) + (0.080P)^2]$
1982 reflections	where $P = (F_o^2 + 2F_c^2)/3$
223 parameters	$(\Delta/\sigma)_{max} < 0.001$
	$\Delta\rho_{max} = 0.20$ e Å^{-3}
	$\Delta\rho_{min} = -0.23$ e Å^{-3}

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O17—H17···O28^i	0.87 (4)	1.74 (4)	2.609 (3)	174 (4)
O27—H27···O18^{ii}	0.83 (4)	1.78 (4)	2.602 (3)	175 (4)

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

Polymorph (III)

Crystal data

$C_9H_{11}NO_2$	$Z = 4$
$M_r = 165.19$	$D_x = 1.337$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 9.6507$ (11) Å	Cell parameters from 1288
$b = 9.8918$ (11) Å	reflections
$c = 10.0082$ (10) Å	$\theta = 2.2$–26.8°
$\alpha = 76.118$ (6)°	$\mu = 0.10$ mm^{-1}
$\beta = 67.655$ (7)°	$T = 173$ (2) K
$\gamma = 69.334$ (9)°	Plate, colorless
$V = 820.61$ (15) Å^3	$0.30 \times 0.20 \times 0.10$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	$R_{int} = 0.059$
	$\theta_{max} = 27.5°$
φ and ω scans	$h = -11 \rightarrow 12$
5655 measured reflections	$k = -12 \rightarrow 12$
3506 independent reflections	$l = -12 \rightarrow 12$
1717 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.052$	
$wR(F^2) = 0.142$	
$S = 0.85$	$w = 1/[\sigma^2(F_o^2) + (0.07P)^2]$
3506 reflections	where $P = (F_o^2 + 2F_c^2)/3$
235 parameters	$(\Delta/\sigma)_{max} < 0.001$
	$\Delta\rho_{max} = 0.21$ e Å^{-3}
	$\Delta\rho_{min} = -0.28$ e Å^{-3}

organic compounds

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

$D—H \cdots A$	$D—H$	$H \cdots A$	$D \cdots A$	$D—H \cdots A$
O17—H17$\cdots$O18^{iii}	0.93 (6)	1.70 (7)	2.607 (2)	164 (4)
O18—H18$\cdots$O17^{iii}	0.83 (9)	1.80 (9)	2.607 (2)	166 (7)
O27—H27$\cdots$O28^{iv}	0.89 (7)	1.71 (7)	2.603 (2)	173 (5)
O28—H28$\cdots$O27^{iv}	0.84 (9)	1.77 (9)	2.603 (2)	175 (6)

Symmetry codes: (iii) $-x+1, -y, -z+2$; (iv) $-x+2, -y, -z+2$.

H atoms were assigned to idealized positions and were allowed to ride, except for the carboxylic acid H atom, whose coordinates were allowed to refine. Neither data set was corrected for absorption [the linear absorption coefficients were 0.09 and 0.10 mm^{-1} for polymorphs (II) and (III), respectively]. For (III), initial structural models included a single protonation site for the two unique carboxylic acids. Difference electron-density maps, as well as the nearly identical C—O bond distances, indicated disorder of the acid H atom across the two O atoms of each acid. To accommodate this disorder, H atoms were placed on the difference peaks and the total occupancy for the two H atoms of each unique acid was constrained to 1. Distance restraints and damping were applied for the initial stages of refinement; these were both relaxed and eventually removed. For both molecules, refinement led to a nearly equal ratio of H-atom populations.

For both compounds, data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

References

Aakeröy, C. B., Beatty, A. M. & Helfrich, B. A. (2001). *Angew. Chem. Int. Ed.* **40**, 3240–3242.

Aakeröy, C. B., Beatty, A. M., Helfrich, B. A. & Nieuwenhuyzen, M. (2003). *Cryst. Growth Des.* **3**, 159–165.

Aakeröy, C. B., Desper, J. & Helfrich, B. A. (2004). *CrystEngComm*, **6**, 19–24.

Anulewicz, A., Hafelinger, G., Krygowski, T. M., Regelmann, C. & Ritter, G. (1987). *Z. Naturforsch. Teil B*, **42**, 917–927.

Bott, R. C., Smith, G., Wermuth, U. D. & Dwyer, N. C. (2000). *Aust. J. Chem.* **53**, 767–777.

Bruker (1997). *SHELXTL.* Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (1999). *SMART* (Version 5.060) and *SAINT* (Version 6.02). Bruker AXS Inc., Madison, Wisconsin, USA.

Domenicano, A., Schultz, G., Hargittai, I., Colapietro, M., Portalone, G., George, P. & Brock, C. W. (1990). *Struct. Chem.* **1**, 107–122.

Etter, M. C. (1990). *Acc. Chem. Res.* **23**, 120–126.

Etter, M. C. & Frankenbach, G. M. (1989). *Chem. Mater.* **1**, 10–12.

Grabowski, S., Delaplane, R. G. & Olavsson, I. (2001). *J. Mol. Struct.* **597**, 67–71.

Hanton, L. R., Hunter, C. A. & Purvis, D. H. (1992). *J. Chem. Soc. Chem. Commun.* pp. 1134–1136.

Kanters, J. A., Kroon, J., Hooft, R., Schouten, A., van Schijndel, J. A. M. & Brandsen, J. (1991). *Croat. Chem. Acta*, **64**, 353–370.

Pedireddi, V. R., Ranganathan, A. & Chatterjee, S. (1998). *Tetrahedron Lett.* **39**, 9831–9834.

Prince, P., Fronczek, F. R. & Gandour, R. D. (1991). *Acta Cryst.* C**47**, 895–898.

Sharma, C. V. K., Panneerselvam, K., Pilati, T. & Desiraju, G. R. (1992). *Chem. Commun.* pp. 832–833.

Sharma, C. V. K., Panneerselvam, K., Pilati, T. & Desiraju, G. R. (1993). *J. Chem. Soc. Perkin Trans. 2*, pp. 2209–2216.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL97.* University of Göttingen, Germany.

Vyas, M., Sakore, T. D. & Biswas, A. B. (1978). *Acta Cryst.* B**34**, 1366–1368.