

# Crystal and molecular structure of 3-dimethylaminobenzoic acid<sup>1</sup>

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The title compound  $C_9H_{11}NO_2$  is triclinic, space group  $P\bar{1}$ , with the cell dimensions  $a = 7.022(1)$ ,  $b = 7.476(2)$ ,  $c = 8.957(1)$  Å,  $\alpha = 87.02(2)$ ,  $\beta = 110.88(1)$ ,  $\gamma = 99.10(1)^\circ$ ,  $V = 433.8(4)$  Å<sup>3</sup>,  $Z = 2$ ,  $M_r = 165.2$ ,  $D_o = 1.27$ ,  $D_x = 1.26$  mg/m<sup>3</sup>,  $F(000) = 176$ ,  $T = 293$  K,  $R = 0.057$  for 939 observed reflections. The molecules are packed as centrosymmetric hydrogen bonded dimers with an O—H  $\cdots$  O distance of 2.626(3) Å. The COOH group is rotated by 1.7(1)° about the exocyclic C(1)—C(7) bond out of the benzene ring plane. The molecules lie on (0 2 - 1) plane for which the  $d$  value is found to be 3.378 Å which is very close to the mean separation between the parallel packed benzene rings [3.347(4) Å]. The entire molecule is planar except for the two methyl groups attached to the nitrogen atom. The N atom is free from any binding of either type C—H  $\cdots$  N or O—H  $\cdots$  N.

## Introduction

3-Dimethylaminobenzoic acid is a simple substituted benzene derivative. The structure was unsolved until now possibly due to so called "chicken wire" problem. The structure was elucidated by using modified method for solving difficult structures using MULTAN-78 (Tavale and Guru Row, 1986).

## Experimental

Needles of  $C_9H_{11}NO_2$  were obtained from ethanol-water mixture. Crystal data:  $M_r = 165.2$ , triclinic, space group  $P\bar{1}$ ,  $a = 7.022(1)$ ,  $b = 7.476(2)$ ,  $c = 8.957(1)$  Å,  $\alpha = 87.02(2)$ ,  $\beta = 110.88(1)$ ,  $\gamma = 99.10(1)^\circ$ ,  $V_c = 433.8(4)$  Å<sup>3</sup>,  $CuK\alpha$  radiation,  $\lambda = 1.5418$  Å,  $\mu = 0.89$  cm<sup>-1</sup>,  $T = 293$  K,  $Z = 2$ , crystal size  $0.1 \times 0.27 \times 0.45$  mm. Lattice parameters were refined from 25 machine centered reflections with  $22 < \theta < 58^\circ$ . Reflections were measured with an index range of  $h$  0/

$7, k \pm 8, l \pm 10$ , using  $\omega/2\theta$  scan mode, scan speed  $1^\circ$  min<sup>-1</sup>, on CAD-4F-11M diffractometer. Three standard reflections ( $-2, -2, -1$ ;  $3, -2, -1$ ;  $-1, 0, 5$ ) measured every 70 measurements of 1345 reflections collected within  $\theta$  range of 0 to  $60^\circ$ , 939 reflections  $|F_o|^2 > 3\sigma|F_o|^2$  were used in the final refinement of structural parameters. No correction for absorption applied.

## Structure determination

A default run using MULTAN-78 (Main *et al.*, 1978) gave a chicken wire. One of the ring atoms was fixed at (O O O) and the other ring atoms shifted accordingly without changing the orientation of the ring. A Fourier map was computed in  $P1$  space group. The centre of symmetry was located and the same was taken as the new origin. Next Fourier gave the entire molecule. A similar procedure can in principle be followed for any other space group after converting the data to triclinic system.

A full-matrix refinement (Gantzel *et al.*, 1961) of scale factor, positional and anisotropic thermal parameters for non-hydrogen atoms (H atoms geometrically fixed and refined isotropically) converged to  $R = 0.057$ ,

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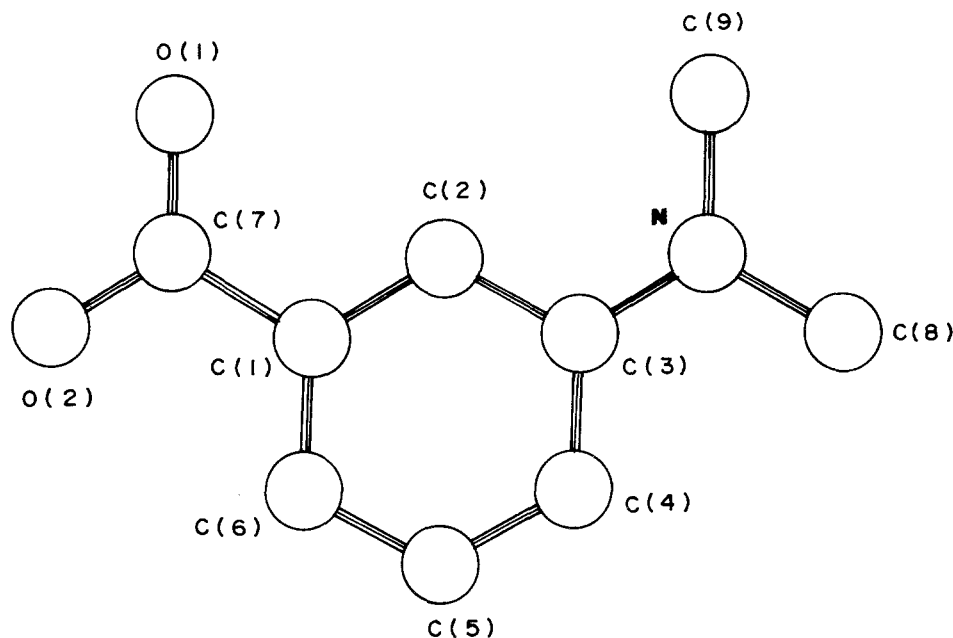


Fig. 1. PLUTO drawing (Motherwell and Clegg, 1978) of the molecule.

$wR = 0.059$ . The function minimized was  $\Sigma w(|F_o| - |F_c|)^2$  with weight of the form  $w = (3.0 + 1.0|F_o| + 0.025|F_o|^2)^{-1}$ . Atomic scattering factors were from International Tables for X-ray crystallography (1974).  $(\Delta/\sigma)_{\max} = 0.1$ , final  $\Delta\rho$  excursions  $< |0.2| \text{ e}\text{\AA}^{-3}$ . No corrections for secondary extinction. All computations were performed on NEC-1000 computer.

## Discussion

Fig. 1 gives a perspective view of the molecule (PLUTO; Motherwell and Clegg, 1978) along with the numbering of atoms. The atomic parameters along with their ESD's and equivalent isotropic thermal parameters for non-hydrogen atoms are given in Table 1 and Table 2 gives the bond lengths and angles.

The phenyl ring atoms are coplanar with  $\pm 0.004 \text{ \AA}$  with C—C bond lengths varying from 1.378(5) to 1.409(4)  $\text{\AA}$  and endocyclic C—C—C angles from 116.6(3) to 121.6(3) $^\circ$  (mean being 1.392  $\text{\AA}$  and 120.0 $^\circ$ ). C—N [1.371(5), 1.451(5), 1.441(5)  $\text{\AA}$ ] and C—O distances [1.241(4), 1.282(4)  $\text{\AA}$ ] are comparable to those found in the structure of p-dimethylaminobenzoic acid (Vyas *et al.*, 1978). The COOH group is rotated by 1.7(1) $^\circ$  about the exocyclic C(1)—C(7) bond out of the benzene ring plane. The entire molecule is

planar except for the two methyl atoms C(8) and C(9) which are displaced by 0.135(4) and 0.120(4)  $\text{\AA}$  in the same direction with respect to the benzene plane. The distances of the H atoms involved in hydrogen bond formation is O(2)—H = 1.24(5), O(1) [1 - x, 1 - y, 2 - z]—H = 1.39(5)  $\text{\AA}$  and O(2)—H—O(1) angle is 171.8(4) $^\circ$ . Similar O—H distances are observed in m-hydroxybenzoic acid (Gridunova *et al.*, 1982) [1.15,

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters for nonhydrogen atoms with ESD's in parentheses  $B_{\text{eq}} = \frac{8}{3} \pi^2 \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* a_i \cdot a_j$

	X	Y	Z	$B_{\text{eq}}$ ( $\text{\AA}^2$ )
C(1)	502(4)	3314(4)	7092(3)	3.90(9)
C(2)	545(4)	2903(4)	5617(3)	4.07(9)
C(3)	-1283(5)	2286(4)	4344(4)	4.41(9)
C(4)	-3127(5)	2092(5)	4659(4)	5.23(11)
C(5)	-3146(5)	2513(5)	6134(4)	5.41(11)
C(6)	-1327(5)	3129(5)	7382(4)	4.73(10)
C(7)	2474(5)	4013(4)	8374(3)	4.05(9)
C(8)	-3090(6)	1066(5)	1643(4)	6.45(13)
C(9)	683(6)	1922(5)	2647(4)	5.67(12)
N	-1249(4)	1961(4)	2861(3)	3.96(9)
O(1)	4112(3)	4226(3)	8108(2)	5.33(8)
O(2)	2387(3)	4369(3)	9731(2)	5.61(8)

**Table 2.** Bond distances (Å) and bond angles (°) with ESD's in parentheses

C(1)—C(2)	1.384(4)		
C(1)—C(6)	1.383(5)		
C(1)—C(7)	1.486(4)		
		C(2)—C(1)—C(6)	121.6(3)
		C(2)—C(1)—C(7)	118.6(3)
		C(6)—C(1)—C(7)	119.8(3)
C(2)—C(3)	1.409(4)	C(1)—C(2)—C(3)	121.1(3)
C(3)—C(4)	1.406(5)		
C(3)—N	1.371(4)	C(2)—C(3)—C(4)	116.6(3)
		C(2)—C(3)—N	121.1(3)
		C(4)—C(3)—N	122.3(3)
C(4)—C(5)	1.378(5)	C(3)—C(4)—C(5)	121.6(3)
C(5)—C(6)	1.394(5)		
		C(4)—C(5)—C(6)	121.2(3)
		C(1)—C(6)—C(5)	117.8(3)
C(7)—O(1)	1.241(4)		
C(7)—O(2)	1.282(4)	C(1)—C(7)—O(1)	120.0(3)
		C(1)—C(7)—O(2)	117.2(3)
		O(1)—C(7)—O(2)	122.8(3)
C(8)—N	1.451(5)		
C(9)—N	1.441(5)	C(3)—N—C(8)	119.9(3)
		C(3)—N—C(9)	120.2(3)
		C(8)—N—C(9)	116.7(3)

**Table 3.** Short intermolecular contacts  $\approx$  less than 3.5 Å

O(1) $\cdots$ C(5)	3.452(4) <sup>a</sup>
C(1) $\cdots$ C(3)	3.503(5) <sup>b</sup>
C(1) $\cdots$ N	3.488(4) <sup>b</sup>
C(7) $\cdots$ N	3.289(4) <sup>b</sup>
N $\cdots$ O(2)	3.502(4) <sup>b</sup>
C(2) $\cdots$ C(2)	3.381(4) <sup>b</sup>
C(7) $\cdots$ O(1)	3.385(4) <sup>c</sup>
C(7) $\cdots$ O(2)	3.440(4) <sup>c</sup>
O(1) $\cdots$ O(1)	3.365(3) <sup>c</sup>
O(2) $\cdots$ O(2)	3.505(4) <sup>c</sup>
C(8) $\cdots$ C(8)	3.451(4) <sup>d</sup>

<sup>a</sup>1 + X, Y, Z.<sup>b</sup>—X, 1 — Y, 1 — Z.<sup>c</sup>1 — X, 1 — Y, 2 — Z.<sup>d</sup>—X — 1, —Y, —Z.

1.47 Å and 172(4)°]; Benzoic acid (Bruno and Randaccio, 1980) [1.29 and 1.35 Å] and several other references (Schuster *et al.*, 1976). The molecules are packed as centrosymmetric hydrogen bonded dimers with O—H  $\cdots$  O distance of 2.626(3) Å whereas nitrogen atom is free from bonding of either type O—H  $\cdots$  N or C—H  $\cdots$  N. The molecules lie on (0 2 — 1) plane for which *d* value calculates as 3.378 Å which is close to the mean separation between the parallel benzene rings [3.347(4) Å]. A list of other short intermolecular contacts  $\approx$  less than 3.5 Å are listed in Table 3.

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Structure factor data have deposited with the British Library, Boston Spa, Whetherby, West Yorkshire, UK, as supplementary publication no. 63115 (10 pages).