Short Communications

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The structure of *N*-methylanthranilic acid.* By N. N. Dhaneshwar and L. M. Pant, *National Chemical Laboratory, Poona, India*

The crystals of *N*-methylanthranilic acid, $NHCH_3C_6H_4COOH$, are monoclinic, space group $P2_1/c$ with $a=8\cdot15$, $b=15\cdot09$, $c=7\cdot03$ Å; $\beta=118\cdot3°$; ϱ_o, $1\cdot307$ g.cm^{-3}; ϱ_c (for $Z=4$), $1\cdot319$ g.cm^{-3}. The structure was refined by the method of least squares resulting in an R value of $0\cdot101$ for 965 observed reflexions; the estimated standard deviations in bond lengths not involving hydrogen atoms are $0\cdot007$–$0\cdot011$ Å and in bond angles about $0\cdot6°$. There is an intramolecular NH···O hydrogen bond in which the N–O distance is $2\cdot672$ Å and O–H distance, $2\cdot02$ Å. The nitrogen atom departs slightly but probably significantly from the plane containing the attached carbon and hydrogen atoms; the $C-NHCH_3$ bond length is $1\cdot373\pm0\cdot008$ Å.

The structure analysis of *N*-methylanthranilic acid (*o*-methylaminobenzoic acid) was undertaken in order to compare its structure with those of anthranilic acid (Brown, 1968) and other related compounds. In particular, it is of interest to study the configuration of the methylamino group and the degree of double bond character of the $C-NHCH_3$ bond.

The crystals grown from solution in toluene are monoclinic, space group $P2_1/c$ with $a=8\cdot15$, $b=15\cdot09$, $c=7\cdot03$ Å; $\beta=118\cdot3°$; ϱ_o, $1\cdot307$ g.cm^{-3}; ϱ_c (for $Z=4$), $1\cdot319$ g.cm^{-3}; μ for Cu $K\alpha$, $9\cdot7$ cm^{-1}.

a was measured from eight reflexions having θ between 48 and 82°, b from ten having θ between 45 and 75° and c from seven having θ between 48 and 81°. Graphs were plotted between d_{100}, d_{010} and d_{001} respectively and sin² θ; the extrapolated values of spacings at $\theta=90°$ were used to calculate axial lengths. The average scatter of points from the graphs was $0\cdot005$ for d_{100}, $0\cdot02$ for d_{010} and $0\cdot003$ Å for d_{001}. Angle β was measured from the zero layer Weissen-

berg photograph about the b axis. Data were collected with unfiltered Cu radiation from zero to sixth layer Weissenberg photographs about the a axis and from zero to fifth layer photographs about the c axis; the crystals used for the two sets of photographs had cross-sections $1\cdot5 \times 1\cdot3$ mm and $1\cdot0 \times 1\cdot4$ mm respectively. Of the 972 reflexions, 560 were present in both sets of photographs. The data were processed in the usual way (Takwale & Pant, 1971; hereinafter referred to as paper I); absorption was neglected.

The structure was solved with the help of sharpened Patterson projections and the Harker line $P(0, y, \frac{1}{2})$ assuming plane centrosymmetrical dimers. The parameters of the hydrogen atoms were obtained and the structure was refined (using observed reflexions only) as in paper I. During the final stages, Cruickshank's weighting scheme was used and the atomic parameters of the hydrogen atoms were also refined although their thermal parameters were kept constant and were assumed to be the same as those of the heavy atoms (C, O, or N) to which they are attached. Final R for 965 observed reflexions was $0\cdot101$; seven reflexions were left out by oversight. The final atomic and

Table 1. *Final atomic and thermal parameters and their standard deviations* (*in parentheses*)

Anisotropic thermal parameters are of the form

$$T=\exp\left[-(b_{11}h^2+b_{22}k^2+b_{33}l^2+2b_{12}hk+2b_{23}kl+2b_{13}hl)\right].$$

(*a*) Non-hydrogen atoms ($\times 10^4$)

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{23}	b_{13}
C(1)	1420 (7)	905 (3)	−3482 (8)	223 (11)	43 (2)	269 (13)	− 3 (4)	− 1 (5)	114 (10)
C(2)	126 (7)	1372 (3)	−5352 (9)	229 (11)	42 (2)	294 (15)	− 3 (4)	− 6 (5)	120 (11)
C(3)	871 (8)	1737 (4)	−6675 (10)	267 (13)	60 (3)	333 (16)	8 (5)	28 (6)	153 (13)
C(4)	2667 (10)	1627 (5)	−6200 (11)	331 (17)	68 (4)	437 (22)	−10 (6)	20 (8)	218 (17)
C(5)	3907 (9)	1142 (5)	−4442 (12)	263 (14)	69 (4)	439 (21)	−11 (6)	7 (7)	182 (15)
C(6)	3259 (8)	785 (4)	−3060 (10)	230 (12)	58 (3)	355 (18)	5 (5)	14 (6)	109 (13)
C(7)	808 (8)	541 (4)	−1945 (8)	244 (12)	51 (3)	251 (13)	3 (4)	2 (5)	98 (11)
C(8)	−3052 (10)	1922 (5)	−7799 (11)	312 (16)	84 (4)	383 (21)	39 (7)	48 (8)	169 (16)
O(1)	2113 (6)	112 (3)	− 274 (6)	274 (10)	73 (2)	305 (11)	22 (4)	36 (4)	132 (9)
O(2)	− 779 (6)	618 (3)	−2180 (6)	267 (9)	67 (2)	291 (11)	15 (4)	32 (4)	133 (9)
N	−1695 (6)	1493 (3)	−5855 (7)	239 (10)	60 (2)	290 (13)	15 (4)	24 (5)	124 (10)

thermal parameters along with the e.s.d.s (obtained from the diagonal terms of the least-squares inverse matrices) are given in Table 1; for brevity, the table of F_o and F_c has been omitted.

Table 1 (cont.)

(b) Hydrogen atoms ($\times 10^3$)

	x	y	z
H(1)	401 (9)	44 (5)	−184 (11)
H(2)	543 (10)	105 (5)	−421 (12)
H(3)	280 (10)	191 (5)	−707 (13)
H(4)	25 (9)	205 (5)	−775 (12)
H(5)	207 (10)	− 24 (5)	44 (11)
H(6)	−266 (10)	259 (5)	−812 (12)
H(7)	−359 (11)	140 (5)	−903 (12)
H(8)	−426 (10)	192 (6)	−759 (12)
H(9)	−227 (9)	121 (5)	−508 (11)

Fig.2. Structure of N-methylanthranilic acid projected on (001).

H(6)–C(8)–H(8)=114°

N–C(8)–H(7)=105°

Fig.1. Bond lengths and angles in N-methylanthranilic acid.

The intramolecular bond lengths and angles are shown in Fig. 1 and listed in Table 2; the e.s.d.'s are the error estimates from the least-squares refinement. The corrections to C(7)–O(1), C(7)–O(2), C(2)–N and N–C(8) bond distances due to librational effects were evaluated as in paper I and amounted to 0·011, 0·009, 0·008 and 0·015 Å respectively; the details of the atomic thermal vibration ellipsoids have been omitted for the sake of brevity. The observed root mean square displacements of atoms C(7), O(1) an O(2) imply an r.m.s. amplitude of oscillation of the carboxylic group about the C(1)–C(7) bond of about 9°. The equations of the various planes referred to the a', b, c orthogonal axes, the angles between them and the deviations of the atoms from the different planes are given in Table 3. The aromatic ring is planar within 0·02 Å; the parallel bonds C(1)–C(2) and C(4)–C(5) of the ring are bent out of the plane by about 1° in opposite directions (Table 3). The atom C(1) and the carboxylic group are coplanar within experimental error but this plane is bent out of the aromatic plane; there is no significant rotation about the C(1)–C(7) bond.

The C–NHCH$_3$ distance, 1·373±0·008 Å (1·365 Å without correction for librational effects) is close to the C–NH$_2$ distances in 2-amino-3-methylbenzoic acid, 1·367±0·002

Table 2. Intramolecular bond lengths and angles

Bond lengths				Bond angles	
	Uncorrected	Corrected	E.s.d.		
C(1)–C(2)	1·422 Å		0·008 Å	C(6)–C(1)–C(2)	120·8 (5)°
C(2)–C(3)	1·439		0·008	C(1)–C(2)–C(3)	115·6 (5)
C(3)–C(4)	1·348		0·010	C(2)–C(3)–C(4)	122·3 (6)
C(4)–C(5)	1·378		0·011	C(3)–C(4)–C(5)	122·4 (7)
C(5)–C(6)	1·414		0·010	C(4)–C(5)–C(6)	117·7 (7)
C(6)–C(1)	1·395		0·008	C(5)–C(6)–C(1)	121·2 (6)
C(1)–C(7)	1·492		0·008	C(1)–C(2)–N	123·0 (5)
C(7)–O(1)	1·321	1·332 Å	0·007	C(3)–C(2)–N	121·4 (5)
C(7)–O(2)	1·229	1·238	0·007	C(2)–N——C(8)	123·9 (6)
C(2)–N	1·365	1·373	0·008	O(1)–C(7)–O(2)	121·2 (5)
N——C(8)	1·441	1·456	0·009	C(1)–C(7)–O(2)	124·0 (5)
O(1)–O(2)*	2·673		0·006	C(1)–C(7)–O(1)	114·8 (5)

* O(1) is at position (x,y,z), O(2) at position $(\bar{x},\ \bar{y},\ \bar{z})$.

Table 2 (cont.)

	Un-corrected	E.s.d.
O(2)–N	2·672	0·007
C(6)–H(1)	0·94	0·08
C(5)–H(2)	1·18	0·08
C(4)–H(3)	0·79	0·08
C(3)–H(4)	0·83	0·08
N—H(9)	0·97	0·07
O(1)–H(5)	0·74	0·08
C(8)–H(6)	1·11	0·08
C(8)–H(7)	1·09	0·09
C(8)–H(8)	1·07	0·08
O(2)–H(9)	2·02	0·07

Table 3. Equations of planes

(1) Benzene ring

$$0·2530x + 0·8410y + 0·4783z + 0·0419 = 0$$

(2) Carboxylic group

$$0·2651x + 0·8515y + 0·4526z - 0·0890 = 0$$

(3) Plane through C(2), N and C(8)

$$0·2330x + 0·8822y + 0·4092z - 0·2892 = 0$$

Angles between different planes

	(2)	(3)
(1)	1·3°	4·8°
(2)	–	3·4

Deviations of atoms from different planes (Å)

	Planes (1)	(2)	(3)
C(1)	0·016	−0·012	−0·072
C(2)	−0·016	—	0·000
C(3)	0·001	—	0·112
C(4)	0·015	—	—
C(5)	−0·014	—	—
C(6)	−0·001	—	—
C(7)	0·072	0·000	—
C(8)	−0·129	—	0·000
O(1)	0·085	0·000	—
O(2)	0·096	0·000	—
N	−0·025	—	0·000
H(1)	−0·03	—	—
H(2)	−0·06	—	—
H(3)	0·08	—	—
H(4)	0·04	—	—
H(5)	−0·12	−0·22	—
H(6)	0·61	—	0·79
H(7)	−1·20	—	−1·05
H(8)	−0·06	—	0·04
H(9)	−0·12	—	−0·15

Å (uncorrected; Brown & Marsh, 1963) and in p-nitro-aniline, 1·371 ± 0·007 Å (uncorrected value, 1·353 Å; Trueblood, Goldish & Donohue, 1961); it is a little longer in the two crystallographically independent molecules of p-aminobenzoic acid, 1·378 ± 0·006 and 1·382 ± 0·006 Å (uncorrected; Lai & Marsh, 1967), and in the molecule of p-methyl-m-nitro-N-methylaniline, 1·377 ± 0·006 Å (uncorrected; Chiaroni, 1971). In the structure of anthranilic acid (Brown, 1968), there are two crystallographically independent molecules; one of them is neutral while the other is a zwitterion. The C–N distance in the zwitterion is as expected much longer, 1·501 ± 0·006 Å (uncorrected) but its value in the neutral molecule, 1·371 ± 0·006 Å (uncorrected) is close to that in N-methylanthranilic acid. The nitrogen atom in N-methylanthranilic acid departs slightly but probably significantly from the plane containing the attached carbon and hydrogen atoms.

The hydrogen atom H(9) attached to the nitrogen atom is involved in an intramolecular NH···O hydrogen bond in which the N–O distance is 2·672 Å; the corresponding distances in other similar structures are: 2·706 Å in 2-amino-3-methylbenzoic acid, 2·685 Å in neutral anthranilic acid and 2·613 Å in the zwitterion, and 2·679 Å in 3·5 dichloroanthranilic acid (Arora & Pant, 1969; the value is not quoted in the paper). The O(2)–H(9) distance, 2·02 ± 0·08 Å agrees with the corresponding distance in 2-amino-3-methylbenzoic acid, 2·05 Å.

The arrangement of molecules in the unit cell is shown in Fig. 2, in which the principal intermolecular distances (< 4·0 Å) are also given.

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The crystal structure of lillianite. By JUNKOU TAKAGI and YOSHIO TAKÉUCHI, Mineralogical Institute, Faculty of Science, University of Tokyo, Hongo, Tokyo

The crystal structure of lillianite, $3PbS.Bi_2S_3$, has been reinvestigated by the symbolic addition method. The result has fully confirmed the structural scheme proposed by Otto & Strunz (Neues Jb. Miner. Abh. (1968). 108, 1). Refinement to an $R = 0·10$ has revealed the mode of distortions characteristic of the structure.

Of the crystalline phases in the system $PbS–Bi_2S_3$, the lead-rich members have structures consisting of fragments of the galena-type structure. The dimensions of the fragments and the way of joining the fragments to form a structure vary according to the Bi_2S_3 to PbS ratio. Takéuchi & Sadanaga (1969) have suggested that the variations would be explainable in terms of the difference in distortions of the fragments due to replacement by Bi of Pb atoms.