SHORT COMMUNICATIONS

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The crystal structure of a second modification of *m*-nitrobenzoic acid.*

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The crystals are monoclinic, space group $P2_1/n$, with a = 7·78 (1), b = 11·15 (1), c = 17·15 (1) Å; β = 93·4 (3)°; ϱ_o = 1·498 g cm^{-3}; ϱ_c for Z = 8, 1·495 g cm^{-3}. The structure, solved by direct methods with visually estimated data, was refined to an R of 0·099 for 1485 $F_{\rm obs}$. As in the first modification, the structure consists of dimeric units, each consisting of crystallographically independent molecules A and B; however, the nitro groups of the dimer are in the *cis* configuration in this structure. The only significant difference between the molecular dimensions in the two crystal modifications is that the two C–O bonds of the carboxylic group in both A and B are nearly equal in this structure whereas they differ by about 0·04 Å in both A and B in the first modification.

m-Nitrobenzoic acid is known to crystallize in one stable and two unstable forms (Davies & Hartshorne, 1934). The structure of the stable modification has recently been determined [Dhaneshwar, Tavale & Pant, 1974; hereinafter referred to as (I)]. In this communication, the structure of one of the unstable modifications is reported.

Transparent, yellowish crystals grown from aqueous alcohol gradually turn white and opaque in the course of several months. The crystal data, determined as in (I) are given above. Data were collected and processed as in (I) from zero to seventh-layer Weissenberg photographs about the a axis and from zero to ninth-layer photographs about the b axis; the crystals used for the two sets of photographs had cross-sections 0·8 × 0·8 and 0·7 × 0·6 mm^2 respectively.

The structure was solved with 268 normalized structure factors in the Sayre-equation program written by Long (1965), and refined as in (I) by the block-diagonal least-squares method to an R of 0·099 for 1485 observed reflexions. The hydrogen atoms of the carboxylic groups were excluded from the refinement; the final difference maps did not reveal these atoms. Final atomic and thermal parameters with their e.s.d.'s are given in Table 1 and the intramolecular bond lengths and angles in Fig. 1; corrections to some of the bond lengths arising from large non-rigid body vibrations were evaluated as in (I). The equations of the various planes referred to the a', b, c orthogonal axes are given in Table 2 along with the angles between them and the deviations of the atoms from these planes. The packing of the molecules is shown in Fig. 2.‡

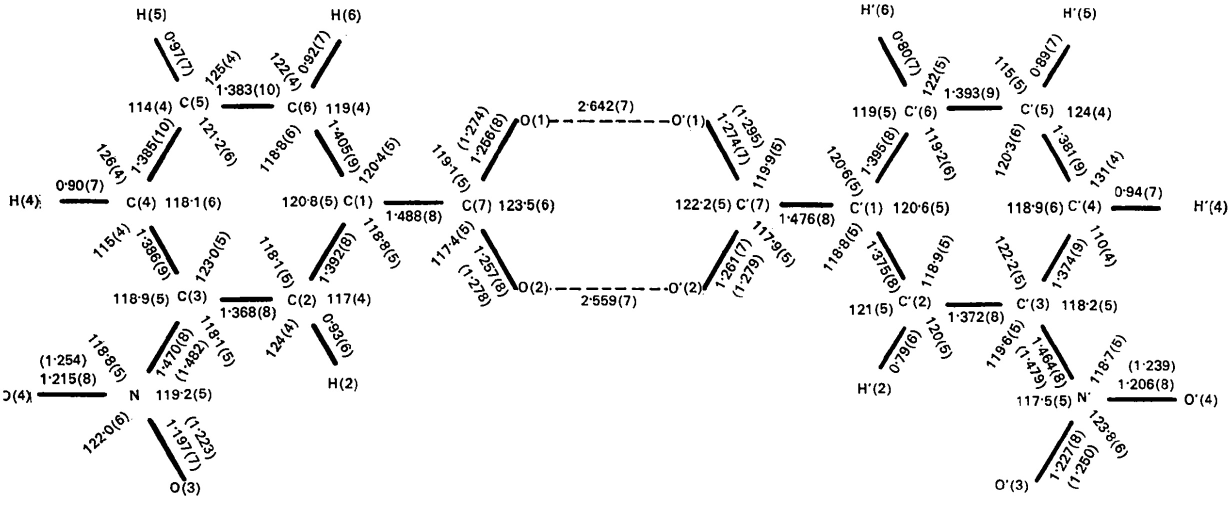

Fig. 1. Bond lengths (Å) and angles (°) with e.s.d.'s; bond lengths in parentheses have been corrected for thermal motion.

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‡ A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30967 (15 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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

Anisotropic thermal parameters are of the form $T=\exp[-(b_{11}h^2+b_{22}k^2+b_{33}l^2+2b_{12}hk+2b_{23}kl+2b_{13}hl)]$.

(*a*) Non-hydrogen atoms (× 10^4)

	x	*y*	*z*	b_{11}	b_{22}	b_{33}	b_{12}	b_{23}	b_{13}
C(1)	−4755 (7)	2486 (5)	4491 (3)	168 (10)	79 (5)	39 (2)	−7 (6)	5 (3)	29 (4)
C(2)	−5208 (7)	1348 (5)	4216 (3)	156 (9)	86 (5)	35 (2)	−4 (6)	−1 (3)	22 (4)
C(3)	−6731 (7)	871 (5)	4428 (3)	165 (10)	86 (5)	36 (2)	−19 (6)	2 (3)	14 (4)
C(4)	−7820 (8)	1461 (6)	4911 (4)	171 (11)	119 (7)	53 (3)	−8 (7)	−5 (4)	43 (5)
C(5)	−7341 (9)	2589 (6)	5184 (4)	215 (13)	119 (7)	61 (3)	−21 (8)	−12 (4)	59 (5)
C(6)	−5832 (8)	3122 (6)	4974 (4)	202 (12)	95 (6)	46 (3)	−14 (7)	−8 (3)	35 (5)
C(7)	−3109 (7)	3023 (6)	4261 (3)	161 (10)	104 (6)	39 (2)	−16 (6)	−7 (3)	21 (4)
O(1)	−2752 (6)	4082 (4)	4460 (3)	233 (9)	95 (4)	61 (2)	−35 (5)	−17 (2)	43 (4)
O(2)	−2130 (6)	2372 (4)	3886 (3)	225 (9)	117 (5)	84 (3)	−51 (6)	−30 (3)	70 (4)
O(3)	−6253 (7)	−860 (4)	3739 (3)	266 (10)	114 (5)	89 (3)	−21 (6)	−35 (3)	47 (5)
O(4)	−8592 (7)	−746 (6)	4297 (4)	284 (12)	204 (8)	98 (3)	−150 (8)	−43 (4)	89 (5)
N	−7218 (7)	−327 (5)	4133 (3)	208 (10)	108 (5)	49 (2)	−46 (6)	−9 (3)	19 (4)
C(1′)	2605 (7)	4846 (5)	3240 (3)	161 (10)	77 (5)	39 (2)	−7 (6)	−2 (3)	20 (4)
C(2′)	3650 (7)	4082 (5)	2853 (3)	161 (10)	77 (5)	43 (2)	−7 (6)	7 (3)	16 (4)
C(3′)	5149 (7)	4520 (5)	2580 (3)	165 (10)	83 (5)	41 (2)	10 (6)	4 (3)	24 (4)
C(4′)	5642 (8)	5696 (6)	2682 (4)	190 (11)	99 (6)	47 (3)	−27 (7)	3 (3)	28 (4)
C(5′)	4578 (8)	6468 (5)	3059 (4)	232 (13)	74 (5)	49 (3)	−23 (7)	5 (3)	31 (5)
C(6′)	3043 (8)	6052 (5)	3339 (4)	254 (14)	75 (5)	46 (3)	−9 (7)	2 (3)	28 (5)
C(7′)	1009 (7)	4368 (5)	3546 (3)	178 (11)	90 (6)	43 (2)	−9 (6)	−2 (3)	28 (4)
O(1′)	78 (6)	5039 (4)	3950 (3)	233 (9)	113 (5)	69 (2)	−6 (5)	−21 (3)	64 (4)
O(2′)	636 (6)	3285 (4)	3408 (3)	224 (9)	98 (4)	69 (2)	−49 (5)	−21 (2)	56 (4)
O(3′)	5863 (7)	2657 (4)	2116 (4)	274 (11)	109 (5)	103 (4)	43 (6)	−15 (3)	55 (5)
O(4′)	7609 (7)	4111 (5)	1948 (4)	219 (10)	170 (7)	114 (4)	−14 (7)	−16 (4)	92 (5)
N′	6292 (7)	3713 (5)	2180 (3)	181 (10)	117 (6)	65 (3)	24 (6)	−3 (3)	32 (4)

Table 1 (*cont.*)

(*b*) Hydrogen atoms (× 10^3)

	x	*y*	*z*
H(2)	−450 (8)	100 (6)	386 (4)
H(4)	−882 (9)	108 (6)	499 (4)
H(5)	−810 (10)	292 (7)	556 (4)
H(6)	−550 (9)	387 (6)	515 (4)
H′(2)	345 (8)	339 (6)	282 (4)
H′(4)	676 (9)	580 (6)	251 (4)
H′(5)	475 (9)	725 (6)	310 (4)
H′(6)	242 (10)	647 (6)	356 (4)

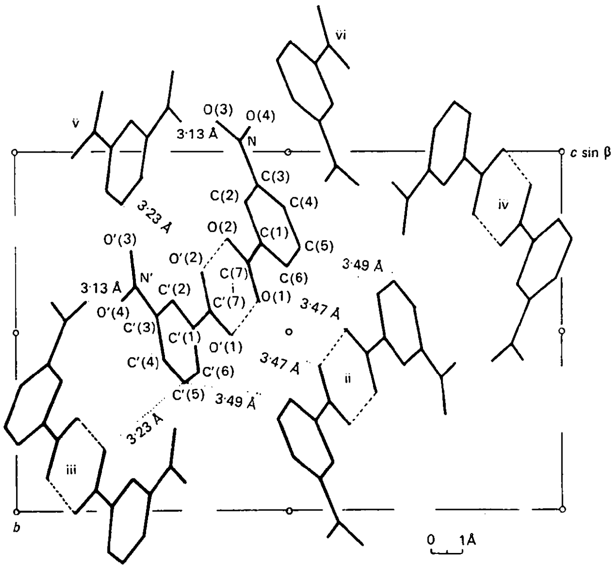


Fig. 2. Structure projected along [100]. Symmetry code: (i) x,y,z; (ii) $\bar{x},1-y,1-z$; (iii) $\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z$; (iv) $\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z$; (v) $\frac{1}{2}-x,y-\frac{1}{2},\frac{1}{2}-z$; (vi) $\bar{x},\bar{y},1-z$.

Table 2. *Equations of planes*

(*a*) Molecule *A*

(1) Benzene ring
$0{\cdot}4790\,X'-0{\cdot}4107\,Y+0{\cdot}7758\,Z'=3{\cdot}2358$ Å
(2) Carboxylic group
$0{\cdot}4517\,X'-0{\cdot}3267\,Y+0{\cdot}8302\,Z'=4{\cdot}0009$
(3) Nitro group
$0{\cdot}4388\,X'-0{\cdot}4132\,Y+0{\cdot}7979\,Z'=3{\cdot}6119$

(*b*) Molecule *B*

(4) Benzene ring
$0{\cdot}4841\,X'-0{\cdot}2290\,Y+0{\cdot}8445\,Z'=4{\cdot}3233$ Å
(5) Carboxylic group
$0{\cdot}5184\,X'-0{\cdot}2798\,Y+0{\cdot}8080\,Z'=3{\cdot}9276$
(6) Nitro group
$0{\cdot}4826\,X'-0{\cdot}2103\,Y+0{\cdot}8502\,Z'=4{\cdot}4298$
(7) Plane through O(1), O(2), O′(1) and O′(2)
$0{\cdot}5055\,X'-0{\cdot}2935\,Y+0{\cdot}8114\,Z'=3{\cdot}8837$

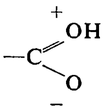
Dihedral angles between planes (°)

	Molecule *A*				Molecule *B*		
	(2)	(3)	(7)		(5)	(6)	(7)
(1)	6·0	2·7	7·2	(4)	4·2	1·3	4·4

Deviations of atoms from planes (Å)

	Molecule *A* planes				Molecule *B* planes		
	(1)	(2)	(3)		(4)	(5)	(6)
C(1)	0·002	0·002		C′(1)	0·010	0·002	
C(2)	0·005			C′(2)	−0·003		
C(3)	−0·006		0·000	C′(3)	−0·006		0·000
C(4)	0·000			C′(4)	0·008		
C(5)	0·008			C′(5)	−0·002		
C(6)	−0·009			C′(6)	−0·007		
C(7)	0·004	−0·007		C′(7)	0·037	−0·008	
O(1)	−0·096	0·002		O′(1)	0·137	0·003	
O(2)	0·132	0·002		O′(2)	−0·012	0·003	
O(3)	0·030		0·000	O′(3)	0·039		0·000
O(4)	−0·066		0·000	O′(4)	0·013		0·000
N	−0·014		0·000	N′	0·006		−0·010
H(2)	−0·070			H′(2)	0·066		
H(4)	−0·053			H′(4)	0·110		
H(5)	0·095			H′(5)	−0·079		
H(6)	−0·012			H′(6)	−0·001		

As in the first modification, the structure consists of dimeric units each consisting of crystallographically independent molecules *A* and *B*; however, unlike the first modification, the nitro groups of the dimer are in the *cis* configuration in this structure (Fig. 2). The dimers are loosely packed and this accounts for the lower density of these crystals (1·498 g cm^{-3}) in comparison with that of the crystals of the first modification (1·519 g cm^{-3}). The dimensions of *A* and *B* are not significantly different. The only difference between the molecular dimensions in the two crystal modifications is that the two C–O bonds of the carboxylic group in both *A* and *B* are nearly equal in the present structure [1·274 (8) and 1·278 (8) Å, and 1·279 (7) and 1·295 (7) Å], whereas they differ by about 0·04 Å in the first modification [1·260 (7) and 1·297 (8) Å, and 1·258 (8) and 1·298 (8) Å]. Apparently, there is less contribution from the structure



in the molecules of the first modification. Presumably because of this, the OH···O hydrogen bonds of the dimers are weaker and longer in the first modification [2·630 (7) and 2·666 (7) Å] than in the present structure [2·559 (7) and 2·642 (7) Å]. A similar difference is observed in the two crystallographically independent dimers of *p*-aminobenzoic acid (Lai & Marsh, 1967). In view of the near equality of the two C–O bonds of the carboxylic group in both *A* and *B* in the present structure, it is probable that the hydrogen atoms forming the dimers are disordered.

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The crystal structure of hydrated cobalt(II) 4-methyltropolonate.

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$P2_1/c$, $a=10{\cdot}147$ (5), $b=25{\cdot}492$ (8), $c=20{\cdot}135$ (8) Å, $\beta=102{\cdot}03$ (4)°; $Z=4$ for $C_{48}H_{52}O_{17}Co_3$. The structure of cobalt(II) 4-methyltropolonate contains both a mononuclear and dinuclear species.

Tropolone, [TH], (Fig. 1, R = H) chelates many metal ions as a singly charged anionic ligand and forms oligomeric crystalline hydrates with Ni(II) and Co(II) (Post, 1971; Irving, Post & Povey, 1973; Irving, Post & Baker, 1975). The compact structure of the ligand (Shimanouchi & Sasada, 1973) is an important factor in the formation and stability of these two compounds. The Co(II) complex with 4-methyltropolone MeTH (Fig. 1, R = CH_3) has been the subject of an investigation into the effect caused by small-group substitutions in the tropolone ring upon the structural behaviour of the ligand. Present results indicate a reduction in packing efficiency.

Small, poorly formed crystals of hydrated Co(II) 4-methyltropolonate were grown from aqueous methanol. The space group was shown to be $P2_1/c$ and cell parameters, from 2θ values of diffractometer centred reflexions, are as given above. A crystal 0·05 × 0·10 × 0·08 mm was mounted for diffractometer data collection with Zr-filtered Mo $K\alpha$ radiation and the θ–2θ scan technique. 918 independent reflexions were measured which had $I \geq 3\sigma(I)$, and these were used in subsequent stages; the inherent resolution of the data was *ca* 1·4 Å. The quality and size of the crystal precluded collection of accurate data to yield a resolution better than this. The structure was solved by direct methods and, following successive full-matrix least-squares refinement and difference syntheses, all the non-hydrogen atoms were placed. Convergence was attained at an R of 0·103† but the paucity of data and the large number of atoms in the asymmetric unit (68 non-hydrogen) caused poorly defined MeT skeletons in two of the ligands.

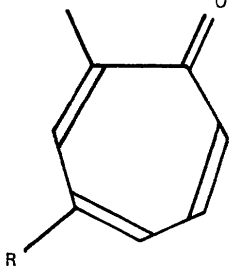

Fig. 1. Chemical diagram of tropolone (R = H) and 4-methyltropolone (R = CH_3).

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† Tables of observed and calculated structure factors and of final atomic positional coordinates and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30960 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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