The Crystal Structure of a Monoclinic Phase of *m*-Nitrophenol

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The structure of monoclinic *m*-nitrophenol, $a=11\cdot240$ (4), $b=6\cdot891$ (2), $c=8\cdot154$ (3) Å, $\beta=98\cdot05$ (3)°, space group $P2_1/n$, has been investigated, in order to answer the question of a possible wrong assignment of the space group. Powdered samples grown from benzene give strong second harmonic generation, whereas no effect is observed in crystals grown from melt; yet their powder diffraction patterns are comparable. The analysis confirmed the centrosymmetric space group; the final unweighted R values for two refinements carried out on data collected with two different crystals, from benzene and from melt, were respectively 0·036 and 0·041. In the crystal hydrogen bonds of moderate strength occur between the hydroxyl and one of the nitro group O atoms (mean O–H$\cdots$O, 2·941 Å). The probable existence of an orthorhombic non-centrosymmetric phase grown from benzene is discussed briefly.

Introduction

Shigorin & Shipulo (1972) have pointed out that *m*-nitrophenol powders, grown from a benzene solution, give strong second harmonic generation (s.h.g.). The only crystallographic information known on this compound is morphological: centrosymmetric monoclinic crystals were described (Barker, 1908; Steinmetz, 1915). On the basis of their measurements Shigorin & Shipulo raised the question of a possible wrong assignment of *m*-nitrophenol as centrosymmetric. Additionally, while testing the acentricity of several samples by means of s.h.g. Coda & Pandarese (1975) found that, whereas crystalline powders of *m*-nitrophenol obtained from benzene and acetone gave strong emission at 0·53 μm, those obtained from melt gave no emission; the powder diffraction patterns of samples from both batches appeared practically the same. A positive piezoelectric effect for *m*-nitrophenol from benzene has been reported (Hettich & Steinmetz, 1932); however we were not able to confirm such an effect with a Wooster instrument, based on the Giebe–Schaube method.

In order to answer the question raised by Shigorin & Shipulo, and to assign the correct space group of this phase, its complete structure determination has been carried out. Two sets of intensities were collected from crystals grown respectively from melt (crystal *A*) and from benzene (crystal *B*); a coarse comparison of the two sets showed that almost certainly their crystal structures were identical. However, separate refinements for *A* and *B* were carried out. This procedure displayed a minor difference between the two crystal crops, *i.e.* a strong secondary extinction effect only for *B*.

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A small amount of non-centrosymmetric phase, never described before, was found in a batch of type *B*, at the end of this investigation; a brief account of it will be given in the concluding remarks.

Some crystallizations from other solvents were also made: crystals grown from water do not exhibit s.h.g.; crystals grown from acetone exhibit s.h.g. stronger than from benzene. Crystals obtained by sublimation behave like those grown from melt: no effect was detected. The dependence of the emission efficiency upon the method of crystallization has not been reported before.

Deuterated *m*-nitrophenol, $m\text{-}NO_2C_6H_4OD$, from benzene, with less than 10% of the non-deuterated compound (the percentage was estimated by n.m.r. spectra) gives a very weak s.h.g.

Experimental

The experimental details and crystal data are given in Table 1. The instrument used for data collection was a Philips PW1100 computer-controlled diffractometer, with the ω–2θ scan technique, equipped with a Mo tube and a graphite monochromator. The cell dimensions were determined with Cu $K\alpha$ radiation by scanning intensities of the $h00$, $0k0$, $00l$, $h0h$ and $h0\bar{h}$ rows, reflected from a small crystal, along both the 2θ circle positive and negative sides for correcting the zero scale error.

The experimental conditions were not identical for *A* and *B*, although they were not too different. Only 902 out of the 1278 reflexions from *A* were considered observable; the remaining 376 reflexions were omitted as they appeared too weak on the basis of the criterion: $I_t - I_b < 2\sqrt{I_t}$, where I_t is the intensity in counts s^{-1}, measured at the top of the scan, and I_b is the mean intensity, in counts s^{-1}, of the preliminary background measurements of 5 s at both sides. The variable scan time for *A* is due to a variable number of scans; they

Table 1. *Crystal and diffraction data*

A: crystal from melt; B: crystal from benzene
$C_6H_5NO_3$, $M = 139.11$
Monoclinic, $a = 11.240$ (4), $b = 6.891$ (2), $c = 8.154$ (3) Å,
$\quad\quad \beta = 98.05$ (3)°, $V = 625.35$ Å³
$D_m = 1.492$ (Steinmetz, 1915), $D_c = 1.477$ g cm⁻³ for $Z = 4$
$F(000) = 288$
Space group $P2_1/n$ (C_{2h}^5), from systematic absences

Crystal dimensions (mm)	A	$0.15 \times 0.18 \times 0.80$
	B	$0.20 \times 0.23 \times 0.85$

Radiation: Mo $K\alpha$, $\lambda = 0.71069$ Å, graphite monochromator
Linear absorption coefficient, Mo $K\alpha$, $\mu = 1.3$ cm⁻¹

Total background counting time, t'	A	$t' = 10$ s
	B	$t' = 20$ s
Scan angular range $\Delta\omega$	A	$\Delta\omega = 1.2°$
	B	$\Delta\omega = 1.5°$
Scan speed v for ω	A	$v = 0.12°$ s⁻¹
	B	$v = 0.03°$ s⁻¹
Measuring time, without background, t (s)	A	$10 \leq t \leq 40$
	B	$t = 50$
θ-range	$\Delta\theta$:	2–$25°$
Number of measured independent reflexions	A:	1278 (376 of them were considered unobservably weak, and skipped)
	B:	1278 (all of them were measured)

Number of intensities with $I \geq n\sigma(I)$ (out of 1278)

	A: $n = 1$	852	B: $n = 1$	1017
	$n = 2$	799	$n = 2$	916
	$n = 3$	726	$n = 3$	880

Room temperature

were repeated until a minimum of 1000 counts was achieved and/or a maximum of four scans performed. 65% of the B intensities were re-measured in a separate run and averaged with the former; this, of course, lowered their standard deviations. The intensities of B are, on the whole, better than those of A; it is worth remembering that this investigation is focused primarily on B, since it was for this crystal that the doubts on the space group were raised.

The crystals decompose slightly during exposure to X-rays; the reference intensities, measured every three hours, decreased, on the average, by 4% per day, and intensities were re-scaled accordingly.

The intensities were corrected for Lorentz and polarization factors, but not for absorption.

Solution and refinement

The coordinates of all non-hydrogen atoms were derived from a Fourier map calculated with 200 reflexions of B with $E \geq 1.27$ phased by *MULTAN* (Germain, Main & Woolfson, 1971). Three cycles of isotropic full-matrix least-squares calculations on these atoms were performed up to convergence; the weighting scheme was based on the experimental $\sigma(F_{obs})$'s de-
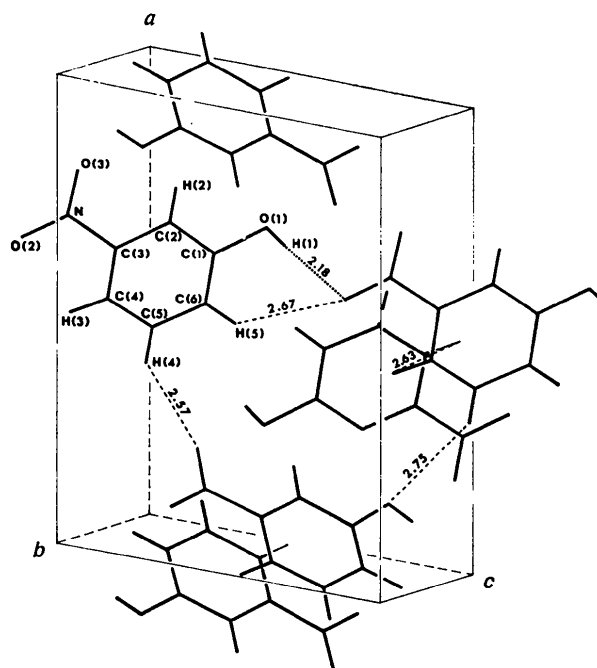

Fig. 1. The unit cell of monoclinic m-nitrophenol. Bond distances are in Å.

Table 2. *Atomic parameters*

Estimated standard deviations are in parentheses. Crystal A: from melt. Crystal B: from benzene (data of better quality).

	A			B		
	x	y	z	x	y	z
C(1)	0.1481 (1)	0.8832 (2)	0.8760 (2)	0.1484 (1)	0.8834 (2)	0.8760 (1)
C(2)	0.1893 (1)	0.9178 (2)	0.7257 (2)	0.1893 (1)	0.9178 (2)	0.7261 (2)
C(3)	0.1236 (2)	0.8425 (2)	0.5848 (2)	0.1240 (1)	0.8430 (2)	0.5849 (1)
C(4)	0.0212 (2)	0.7359 (2)	0.5851 (3)	0.0212 (1)	0.7359 (2)	0.5851 (2)
C(5)	−0.0175 (2)	0.7013 (2)	0.7359 (3)	−0.0170 (1)	0.7014 (2)	0.7367 (2)
C(6)	0.0457 (2)	0.7749 (2)	0.8799 (2)	0.0460 (1)	0.7748 (2)	0.8807 (2)
N	0.1681 (2)	0.8803 (2)	0.4253 (2)	0.1680 (1)	0.8805 (2)	0.4259 (1)
O(1)	0.2145 (2)	0.9619 (2)	1.0128 (2)	0.2141 (1)	0.9607 (2)	1.0135 (1)
O(2)	0.1091 (2)	0.8152 (2)	0.3000 (2)	0.1091 (1)	0.8152 (2)	0.2997 (1)
O(3)	0.2587 (2)	0.9749 (2)	0.4251 (2)	0.2584 (1)	0.9748 (2)	0.4250 (1)
H(1)	0.193 (2)	0.932 (3)	1.072 (4)	0.186 (1)	0.923 (3)	1.086 (3)
H(2)	0.257 (2)	0.999 (2)	0.722 (3)	0.258 (1)	0.988 (2)	0.723 (2)
H(3)	−0.025 (2)	0.689 (2)	0.490 (3)	−0.022 (1)	0.687 (2)	0.484 (2)
H(4)	−0.087 (1)	0.623 (2)	0.739 (3)	−0.087 (1)	0.627 (2)	0.738 (2)
H(5)	0.017 (2)	0.748 (2)	0.974 (3)	0.020 (1)	0.750 (2)	0.984 (2)

rived from the counting statistics, and R dropped from 37 to 17%. The H atoms were located from a difference synthesis, and introduced in the structure-factor calculation. Afterwards the anisotropic B_{ij} of the non-hydrogen and the isotropic B_H of the H atoms were refined, together with their coordinates; three full-matrix least-squares cycles led to $R=4\cdot1\%$ (A) and $5\cdot4\%(B)$. At this stage a conspicuous secondary extinction effect was observed for B by comparison of the calculated and observed amplitudes; after testing that this effect was not an instrumental artifact arising from counter saturation or similar sources, a secondary extinction correction was applied and two additional least-squares cycles yielded an R for B comparable to that already obtained for A: $3\cdot6\%$; a similar correction for A did not produce any improvement, as expected. Secondary extinction correction was based on the formula (14) from Zachariasen (1963), with $C= 4\times10^{-4}$; a more appropriate and accurate correction was not available in our present set of programs. Nevertheless our correction appeared to fit quite well the data of B since a remarkable improvement of the O–H and C–H bond distances was achieved.

The refinement was performed with a locally modified *ORFLS* program (Busing, Martin & Levy, 1963). The scattering factors for the non-hydrogen

atoms were taken from Hanson, Herman, Lea & Skillman (1964); that of H from Stewart, Davidson & Simpson (1965).

The final positional and thermal parameters of A and B and their standard deviations are given in Tables 2 and 3.* The numbering of the atoms is in Fig. 1.

Discussion

The bond lengths and angles of A and B are listed in Table 4; the shortest intermolecular distances are given only for B in Table 5; the distances of all the atoms of B from the benzene plane are reported in Table 6.

The benzene plane and the plane of the nitro group [*i.e.* the best plane fitting C(3), N, O(2) and O(3)] are almost parallel: $0\cdot65\pm0\cdot18°$ (A), $0\cdot52\pm0\cdot15°$ (B); this angle, though small, appears to be significant, since the inclusion of O(2) and O(3) increases the distances of the C atoms from the plane. The corresponding

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Table 3. *Anisotropic thermal parameters*

$$T=\exp\left[-10^4\times(h^2B_{11}+\ldots+hkB_{12}+\ldots)\right].$$

Estimated standard deviations are in parentheses. The figures given in the last column (B_H, in Å²) represent the equivalent thermal parameters (Hamilton, 1959) for the non-hydrogen atoms; for the hydrogens, they represent the isotropic thermal parameters.

Structure A

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B_H
C(1)	72 (1)	174 (4)	72 (2)	1 (2)	14 (1)	1 (3)	2·91
C(2)	67 (2)	178 (4)	92 (3)	−11 (2)	22 (2)	−7 (3)	3·00
C(3)	77 (2)	164 (4)	67 (3)	8 (2)	20 (2)	4 (2)	2·86
C(4)	77 (1)	203 (5)	88 (3)	−5 (2)	−5 (1)	−15 (2)	3·38
C(5)	71 (1)	253 (4)	134 (2)	−33 (2)	14 (1)	5 (3)	3·92
C(6)	79 (2)	237 (5)	92 (3)	3 (2)	34 (2)	20 (3)	3·52
N	107 (2)	196 (4)	83 (3)	21 (2)	34 (1)	0 (3)	3·66
O(1)	112 (1)	366 (5)	68 (3)	−51 (2)	13 (2)	−12 (2)	4·74
O(2)	155 (2)	328 (4)	65 (2)	−2 (2)	13 (2)	−17 (3)	5·21
O(3)	133 (1)	420 (4)	129 (3)	−72 (2)	68 (2)	−22 (3)	5·80

	H(1)	H(2)	H(3)	H(4)	H(5)
B_H	1·8 (6)	3·2 (4)	3·9 (3)	3·5 (4)	3·3 (3)

Structure B

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B_H
C(1)	77 (1)	194 (4)	79 (2)	10 (1)	14 (1)	0 (2)	3·18
C(2)	71 (1)	193 (4)	96 (2)	−9 (2)	23 (1)	−1 (2)	3·20
C(3)	81(1)	163 (3)	80 (2)	16 (2)	24 (1)	7 (2)	3·03
C(4)	83 (1)	215 (4)	102 (2)	0 (2)	2 (1)	−14 (2)	3·65
C(5)	72 (1)	257 (4)	138 (3)	−26 (2)	20 (1)	7 (3)	4·00
C(6)	76 (1)	247 (4)	100 (2)	3 (2)	30 (1)	20 (2)	3·62
N	111 (1)	213 (3)	90 (2)	22 (2)	33 (1)	−2 (2)	3·91
O(1)	110 (1)	346 (4)	81 (2)	−44 (1)	13 (1)	−14 (2)	4·72
O(2)	155 (1)	335 (4)	79 (2)	−2 (1)	15 (1)	−20 (2)	5·38
O(3)	138 (1)	407 (4)	153 (2)	−69 (2)	80 (1)	−22 (2)	5·99

	H(1)	H(2)	H(3)	H(4)	H(5)
B_H	6·4 (5)	3·7 (3)	4·0 (3)	4·0 (3)	4·2 (3)

Table 4. *Interatomic bond lengths* (Å) *and angles* (°)

Estimated standard deviations are in parentheses; the figures for B are more accurate. Symmetry code: see Table 5.

	A	B		A	B
C(1)–C(2)	1·390⁻(3)	1·385⁻(2)	N–O(2)	1·223 (3)	1·228 (2)
C(2)–C(3)	1·377 (3)	1·376 (2)	N–O(3)	1·209 (3)	1·207 (2)
C(3)–C(4)	1·366 (3)	1·371 (2)	O(1)–H(1)	0·60 (3)	0·76 (2)
C(4)–C(5)	1·382 (3)	1·385 (2)	C(2)–H(2)	0·95 (3)	0·92 (2)
C(5)–C(6)	1·381 (3)	1·379 (2)	C(4)–H(3)	0·93 (3)	0·96 (2)
C(6)–C(1)	1·375 (3)	1·378 (2)	C(5)–H(4)	0·95 (3)	0·94 (2)
C(1)–O(1)	1·366 (3)	1·362 (2)	C(6)–H(5)	0·89 (3)	0·94 (2)
C(3)–N	1·480 (3)	1·474ₐ(2)	O(1)···O(2ⁱ)	2·947 (3)	2·935 (2)

	A	B		A	B
C(1)–O(1)–H(1)	106·5 (1·8)	105·5 (1·4)	O(2)–N–O(3)	123·7 (2)	123·2 (1)
C(6)–C(1)–C(2)	119·8 (2)	119·9 (1)	C(3)–C(4)–C(5)	117·7 (2)	117·4 (1)
C(6)–C(1)–O(1)	124·1 (2)	123·3 (1)	C(3)–C(4)–H(3)	124·0 (9)	121·3 (8)
O(1)–C(1)–C(2)	116·1 (2)	116·8 (1)	H(3)–C(4)–C(5)	118·3 (9)	121·3 (8)
C(1)–C(2)–C(3)	117·7 (2)	118·1 (1)	C(4)–C(5)–C(6)	120·3 (2)	120·7 (1)
C(1)–C(2)–H(2)	119·8 (9)	119·9 (8)	C(4)–C(5)–H(4)	118·9 (9)	117·8 (8)
H(2)–C(2)–C(3)	122·3 (9)	122·0 (8)	H(4)–C(5)–C(6)	120·7 (9)	121·5 (8)
C(2)–C(3)–C(4)	123·7 (2)	123·5 (1)	C(5)–C(6)–C(1)	120·8 (2)	120·5 (1)
C(2)–C(3)–N	117·3 (2)	117·7 (1)	C(5)–C(6)–H(5)	116·4 (9)	120·3 (8)
C(4)–C(3)–N	119·0 (2)	118·8 (1)	H(5)–C(6)–C(1)	122·9 (9)	119·2 (8)
C(3)–N–O(2)	117·4 (2)	117·7 (1)	O(1)–H(1)···O(2ⁱ)	179·5 (2·0)	178·1 (1·8)
C(3)–N–O(3)	119·0 (2)	119·1 (1)			

Table 5. *Intermolecular shortest distances for B* (Å)

Only the distances shorter than 3·2 Å are tabulated. Estimated standard deviations are in parentheses.

(i)	$x,$	$y,$	$1+z$	(v)	$\frac{1}{2}+x,$	$\frac{1}{2}-y,$	$-\frac{1}{2}+z$
(ii)	$x,$	$y,$	$-1+z$	(vi)	$\frac{1}{2}-x,$	$\frac{1}{2}+y,$	$\frac{1}{2}-z$
(iii)	$-x,$	$1-y,$	$1-z$	(vii)	$\frac{1}{2}-x,$	$-\frac{1}{2}+y,$	$\frac{1}{2}-z$
(iv)	$\frac{1}{2}+x,$	$\frac{3}{2}-y,$	$\frac{1}{2}+z$				

O(1)···O(2ⁱ)	2·935 (2)	O(3)···H(5ᵛⁱ)	3·13 (2)
O(1)···Nⁱ	3·192 (2)	N·····H(1ⁱⁱ)	2·82 (2)
O(1)···H(3ⁱᵛ)	3·17 (2)	C(1)···H(2ᵛⁱⁱ)	3·07 (2)
O(1)···H(4ⁱᵛ)	2·75 (2)	C(2)···H(2ᵛⁱⁱ)	3·03 (2)
O(2)···H(1ⁱⁱ)	2·18 (2)	C(3)···H(2ᵛⁱⁱ)	3·10 (2)
O(2)···H(4ⁱⁱⁱ)	3·07 (2)	C(4)···H(3ⁱⁱⁱ)	2·97 (2)
O(2)···H(5ⁱⁱ)	2·67 (2)	C(6)···H(2ᵛⁱⁱ)	3·16 (2)
O(3)···H(1ⁱⁱ)	2·79 (2)	H(1)····H(4ⁱᵛ)	2·70 (9)
O(3)···H(1ᵛⁱ)	3·15 (2)	H(3)···H(3ⁱⁱⁱ)	2·63 (9)
O(3)···H(4ᵛ)	2·57 (2)	H(3)···H(4ⁱⁱⁱ)	3·18 (9)

Table 6. *Distances of the atoms from the benzene plane, in structure B* (Å)

Standard deviations are in parentheses.
Equation of the benzene root-mean-square plane, in structure
B: $-6·0524X+5·7571Y-0·2718Z-3·9446=0$

C(1)	0·005 (1)	O(2)	0·007 (1)
C(2)	−0·004 (1)	O(3)	−0·012 (1)
C(3)	−0·001 (1)	H(1)	−0·051 (17)
C(4)	0·004 (1)	H(2)	−0·015 (13)
C(5)	−0·004 (1)	H(3)	0·016 (13)
C(6)	−0·002 (1)	H(4)	−0·007 (13)
O(1)	0·014 (1)	H(5)	−0·018 (12)
N	−0·008 (1)		

angles for *p*-nitrophenol are: 1°32′ for the α (Coppens & Schmidt, 1965*a*), and 7°9′ for the β-modification (Coppens & Schmidt, 1965*b*).

The C–H distances are 0·95, 0·93, 0·95, 0·89 Å (*A*), and 0·92, 0·96, 0·94, 0·94 Å (*B*), with individual

standard deviations ranging between 0·015 and 0·020 Å, and average C–H = 0·935 Å; the O–H distances are 0·60 (*A*) and 0·76 Å (*B*), with $\sigma = 0·02$ Å. These bond lengths are quite short compared with the standard values C–H = 1·11 and O–H = 0·99 Å (Brown & Levy, 1973). However the refinement will shift the location of the H atom toward the atom to which it is bonded because of the large aspherical distortion of the electron density (Hvoslef, 1968; Hanson, Sieker & Jensen, 1973). These authors have found the shift to be nearly 0·1 for C–H and 0·2 Å for O–H. Thus the corresponding O–H distances found in *m*-nitrophenol, although short, compare well with figures given in the literature; several examples of quite short O–H bonds in well refined structures are known: for example 0·66, 0·67, 0·72 and 0·84 Å are reported for a derivative of myoinositol (Cook & Bugg, 1973).

The molecules equivalent by translation along c are linked in an infinite chain through hydrogen bonds of length 2·947 (*A*), 2·935 Å (*B*); the angles O(1)–H(1)–O(2ⁱ) are 179·5 ± 2° (*A*), 178·1 ± 1·8 ° (*B*), and the H(1)···O(2ⁱ) distances are 2·35(*A*), 2·18 Å (*B*): see Table 5 for the key to the symmetry code. The plane (1̄10) cuts almost normally the system of hydrogen bonds which plays a predominant role in the packing. The next shortest distance of O(2) from O(1) is O(1)···O(2ᵛⁱ) = 3·37 Å (*B*) which is too long for a hydrogen bond. O(3) is not involved in any hydrogen bond, as its shortest distances are: O(1)···O(3ⁱ) = 3·32 Å (*B*) and O(1)···O(3ᵛⁱⁱ) = 3·39 Å (*B*).

The van der Waals contacts, O(3)···H(4ᵛ) = 2·57, H(3)···H(3ⁱⁱⁱ) = 2·63, O(2)···H(5ⁱⁱ) = 2·67 and O(1)···H(4ⁱᵛ) = 2·75 Å, are depicted in Fig. 1. The shortest distance not involving H atoms is O(1)···Nᵛⁱ = 3·19 Å.

Conclusions

The space group of the monoclinic phase of m-nitrophenol studied in this investigation can be safely settled as $P2_1/n$. The only significant difference found between the two monoclinic crystals A (from melt) and B (from benzene) is that the latter is considerably affected by secondary extinction, which is negligible in the former. Shigorin & Shipulo (1974) put forward the hypothesis that optical non-linearities in crystals which appear centrosymmetrical from X-ray evidence, could arise from local acentricities, for instance, in the hydrogen-bonding system; the s.h.g. could be inherently more sensitive than X-ray diffraction to the very small deviations involved, say 0·01 Å or less. In the particular case of monoclinic m-nitrophenol, the detailed picture of the structure that has been achieved is not consistent, in our opinion, with an asymmetry located in the hydrogen-bonding system of B. Accordingly the strong s.h.g. of the batch of crystals from benzene cannot be explained by an incorrect assignment of the space group.

During the preparation of the manuscript a systematic determination of crystal data was carried out on many crystals from a batch of type B (*i.e.* grown from benzene), to make sure that another crystal phase, second-harmonic emitting, was not present. It was a happy surprise to find some orthorhombic crystals whose outward appearance and whose lattice constants were very similar to those of the monoclinic phase. A preliminary determination gave $a = 11·305$, $b = 6·777$, $c = 8·123$ Å (to be compared with the monoclinic $a = 11·240$, $b = 6·891$, $c = 8·154$ Å, $\beta = 98·05°$), $Z = 4$ and space group $P2_12_12_1$ from systematic absences. In a rough estimation these crystals appeared to be 20% of the total; they may not have been detected if the s.h.g. had not suggested a very scrupulous check; for instance, they escaped the careful examination of morphologists like Barker (1908) and Steinmetz (1915), who mention benzene and acetone as solvents used to yield m-nitrophenol single crystals. Davies & Hartshorne (1934) found 'occasional individuals with more or less rhombic outlines' amid monoclinic crystals from water and acetone, but did not claim the existence of a new phase.

The crystal structure investigation of orthorhombic m-nitrophenol is now in progress.

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