tions, particularly of the type $00l$, there existed the possibility that the observed characteristic extinctions were fortuitous. Therefore refinements were also performed in space groups $P2_1$ and Pb. In both cases the refinement converged to the same positional parameters and temperature factors as for $P2_1/b$. In addition the general set in both these non-centric space groups is twofold, two such sets being occupied by nickel and two by yttrium. The Busing, Martin & Levy program generates a correlation matrix during the refinement procedure. In both space groups this correlation matrix indicated correlation probabilities of 90–99% between twofold sets containing the same atomic species, and thus the correlation indicates a relationship which generates the fourfold sets of $P2_1/b$.

Discussion

The YNi structure is closely related to the orthorhombic ThNi structure (Florio, Baenziger & Rundle, 1956). The structural relationship can be shown by choosing a double unit cell for YNi with $a = 14\cdot28$, $b = 4\cdot11$, and $c = 5\cdot50$ Å. Then in comparison the ThNi lattice parameters are $a = 14\cdot15$, $b = 4\cdot31$, and $c = 5\cdot73$ Å. The atoms are arranged in this large YNi unit cell in two sets of the type $\pm(xyz; \frac{1}{4}+x, y, \frac{1}{2}-z; \frac{1}{2}+x, y, z; \frac{3}{4}+x, y, \frac{1}{2}-z)$ with $x_{Ni}=0\cdot019$, $y_{Ni}=0\cdot245$, $z_{Ni}=0\cdot622$ and $x_Y=0\cdot090$, $y_Y=0\cdot249$, $z_Y=0\cdot132$. Again in comparison the atoms in the ThNi structure are in two sets of the type $\pm(xyz; \frac{1}{4}+x, y, z; \frac{1}{2}+x, y, \frac{1}{2}-z; \frac{3}{4}+x, y, \frac{1}{2}-z)$ with $x_{Ni}=0\cdot018$, $y_{Ni}=0\cdot250$, $z_{Ni}=0\cdot630$ and $x_{Th}=0\cdot094$, $y_{Th}=0\cdot250$, $z_{Th}=0\cdot140$. Thus a definite structural relationship is evident, the primary difference being in the sequence of the z parameters. A second significant difference is in symmetry with the lower symmetry of YNi resulting from the failure of the atoms to occupy the $y=\frac{1}{4}$ positions.

This failure of the yttrium and nickel atoms to occupy the $\frac{1}{4}$ and $\frac{3}{4}$ positions along the short axis is the only structural feature which differentiates the YNi structure from the $B27$ type structure (Pearson, 1958) typified by FeB (Bjurström & Arnfelt, 1929; Bjurström, 1933). Otherwise, the positional parameters and axial ratios of YNi are quite comparable to known $B27$ structures, and for classification purposes YNi should be included with this latter group.

References

BEAUDRY, B. J. & DAANE, A. H. (1960). *Trans. Amer. Inst. Min. (metall.) Engrs,***218**, 854.
BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1960). U.S. Atomic Energy Commission Report No. ORNL–YM—305.
BJURSTRÖM, T. (1933). Ark. Kem. *11*A, No. 5.
BJURSTRÖM, T. & ARNFELT, H. (1929). *Z. phys. Chem.* B4, 469.
DOMAGALA, R. F., RAUSCH, J. J. & LEVINSON, D. W. (1961). *Trans. Amer. Soc. Met.* **53**, 137.
FLORIO, J. V., BAENZIGER, N. C. & RUNDLE, R. E. (1956). *Acta Cryst.* 9, 367.
NELSON, J. B. & RILEY, D. P. (1945). *Proc. Phys. Soc. Lond.* 57, 160.
PEARSON, W. B. (1958). *Handbook of Lattice Spacings and Structures of Metals and Alloys*, p. 93. New York: Pergamon Press.

The Crystal Structure of the α-Modification of p-Nitrophenol near 90 °K

By PHILIP COPPENS AND G. M. J. SCHMIDT

Department of X-ray Crystallography, Weizmann Institute of Science, Rehovoth, Israel

The crystal structure of the α modification of p-nitrophenol near 90 °K has been determined by the use of partial three-dimensional data. The cell dimensions are $a = 11\cdot66$, $b = 8\cdot78$, $c = 6\cdot098$ Å, $\beta = 107°\,32'$. The space group is $P2_1/n$ and $Z = 4$. The crystals contain chains of hydrogen-bonded molecules. The benzene ring is planar but the nitrogen and oxygen atoms are displaced from the benzene-ring plane by amounts varying from $0\cdot03$–$0\cdot07$ Å.

Introduction

The structure analysis of the α modification of p-nitrophenol (I), started in 1957 and reported in this

(I)
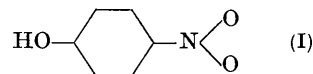
paper, forms part of a research program on the chemistry of the solid state (Schmidt, 1957). The reaction occurring on irradiation of the α modification of p-nitrophenol manifests itself in the irreversible color change of the crystal from yellow to red; it is evidently structure dependent since the β-form is light stable as was first observed by Fritzsche (1859), and checked by us.

The room-temperature structure of the β modification will be described in a subsequent publication.

Experimental

Crystals of the α form can be grown by slow evaporation of solutions of p-nitrophenol in diethyl ether. The crystallographic constants near 300 and 90 °K are listed in Table 1. The cell dimensions compare well with previously reported room temperature values (Toussaint, 1954).

Table 1. *Crystallographic constants of α-p-nitrophenol*

At room temperature
(Toussaint, 1954)   Near 90 °K*

At room temperature (Toussaint, 1954)	Near 90 °K*
$a = 11 \cdot 8$ Å	$a = 11 \cdot 66$ Å
$b = 8 \cdot 9$	$b = 8 \cdot 78$
$c = 6 \cdot 17$	$c = 6 \cdot 098$
$\beta = 106° \ 52'$	$\beta = 107° \ 32'$
$P2_1/n$	$P2_1/n$
$d_c = 1 \cdot 51$ g.cm^{-3} ($Z = 4$)	$d_c = 1 \cdot 551$ g.cm^{-3} ($Z = 4$)

* Cell dimensions determined from Weissenberg photographs, corrected for film shrinkage. Cell edges $\pm 0 \cdot 1\%$, $\beta \pm 6'$.

The $hk0$ and $hk3$ intensities were measured on a needle-shaped crystal of cross section $0 \cdot 4 \times 0 \cdot 4$ mm; for the $h0l$ intensities we used a cube-shaped crystal, with an edge of about $0 \cdot 3$ mm, which had been cut by means of an alcohol-wetted nylon thread. All intensities were recorded at the temperature of boiling nitrogen with an equi-inclination Weissenberg camera (Hirshfeld & Schmidt, 1956) and Ni-filtered Cu K radiation. Intensities, measured visually, ranged from $28,000-1$ for $hk0$, $10,000-1$ for $h0l$, and $2,000-1$ for $hk3$. All usual corrections were applied by means of a computer program; no allowance was made for absorption. Approximate values of the scale factor k and of an average temperature factor were obtained from a Wilson plot (Wilson, 1942).

Solution of the structure

The $[hk0]$ zone was solved (Coppens, Schmidt & Gillis, 1958) by means of the inequality (Harker & Kasper, 1948)

$$(U_H \pm U_{H'})^2 \leq (1 \pm U_{H+H'}) \cdot (1 \pm U_{H-H'}) . \quad (1)$$

The origin of the projection was fixed by the arbitrary assignment of signs to two reflections with h odd and k odd respectively. Systematic application of the inequality (1) by a procedure due to Gillis (1948) led to contradictions which could be eliminated by a 20% reduction of the scale factor k. Subsequently, the signs of seven reflections were established absolutely; the signs of eleven other reflections could be expressed relative to each other. Two electron-density projections $\varrho(xy)$ were computed with these twenty reflections; one of these maps could be interpreted and yielded trial coordinates whose correctness was established by the eventual refinement.

We may note here that unitary structure factors U were recalculated with the final scale and temperature factors. Somewhat surprisingly, their correct values are about half those used in the solution of the structure; the inequalities are now found to be nearly always satisfied by both signs, frequently with a *narrower* margin by the wrong sign (*e.g.* the example given below). Nevertheless, only one out of the eighteen signs determined with the old U's proves to be incorrect. A similar experience has been recorded by Gillis (1948) who noted that the inequalities method had reserves of power in the sense that stronger inequalities than those used were in fact satisfied. He found that, if both signs satisfied an inequality, one by a comfortable margin and the other by a relatively narrow margin, the former sign was almost always the correct one.

An example of a sign determination is given below:

$$|U_{410}| = 0 \cdot 35; \quad |U_{800}| = 0 \cdot 70; \quad |U_{020}| = 0 \cdot 10$$
$$(U_{410} - U_{4\bar{1}0})^2 \leq (1 - U_{800})(1 - U_{020}) \text{ since } U_{410} = -U_{4\bar{1}0}$$

or $0 \cdot 49 \leq (1 - U_{800}) \times 1 \cdot 1$ or $(1 - U_{800}) \geq 0 \cdot 45$ which is only satisfied if U_{800} is negative. (We have assumed U_{020} to be negative, thus choosing the less stringent condition. If U_{020} is taken as positive we get $(1 - U_{800}) \geq 0 \cdot 53$, which is a more powerful result.) The final values are however: $|U_{410}| = 0 \cdot 17$; $|U_{800}| =$

Table 2. *Refinement of the structure*

	Level	$100r$	$\Sigma w \Delta^2/n-s$	Resulting w_0	Number of reflections Observed	Number of reflections Unobserved
Separate level refinement	$hk0$	4·64	0·71	1·0	122	6
	$hk3$	3·04	0·81	1·0	174	20
	$h0l$	3·62	0·58	1·25	77	10
Refinement of all data	—	3·47	0·76	—	358*	35*

w = weight assumed to be equal to w_0/F_o^3, in which w_0 is a constant for each level; $\Delta = k^2F_o^2 - F_c^2$;
n = number of reflections; s = number of parameters.

* These numbers are smaller than the sum of the corresponding values for the separate levels, since the reflections common to two levels were included only once in the refinement.

Table 3. Observed and calculated structure factors

Sign < indicates unobserved reflection

Upper section — group 1

h	k	l	100 F_o	100 F_c
0	2	0	1322	-1290
		4	3723	4569
		6	737	748
		8	340	320
		10	535	-561
1	1	0	1857	-1387
		2	2944	3561
		3	1526	1596
		4	463	-485
		5	2504	-2783
		6	211	-244
		7	1857	1871
		8	<116	-39
		9	786	782
		10	829	-816
		11	585	-602
2	1	0	1028	-1115
		2	5425	-8935
		3	648	-729
		4	443	-366
		5	1748	-1832
		6	1873	-1866
		7	1916	-1900
		8	387	370
		9	125	129
		10	<125	-18
		11	743	716
3	1	0	608	557
		2	2636	2801
		3	604	-638
		4	535	553
		5	496	-482
		6	998	-988
		7	129	-135
		8	228	203
		9	482	-448
		10	387	413
		11	<54	-33
4	1	0	3020	3525
		2	555	-512
		3	538	480
		4	1450	1463
		5	211	209
		6	264	-254
		7	287	292
		8	152	126
		9	545	545
		10	122	110
5	1	0	377	-296
		2	304	284

Upper section — group 2

h	k	l	100 F_o	100 F_c
		3	1249	1269
		4	1331	1297
		5	965	826
		6	119	87
		7	1513	-1400
		8	439	396
		9	198	-185
		10	637	609
6	1	0	1041	1134
		2	1487	1582
		3	1262	-1264
		4	1008	953
		5	1417	1304
		6	1589	1353
		7	1054	-1003
		8	86	-78
		9	162	115
		10	403	387
7	1	0	790	716
		2	1107	-1083
		3	380	334
		4	2118	-2162
		5	2035	1947
		6	968	-792
		7	790	-740
		8	687	-617
		9	244	206
8	1	0	396	350
		2	1483	1336
		3	1272	-1208
		4	1437	-1257
		5	2643	2439
		6	1262	-1164
		7	866	-768
		8	624	-542
		9	416	375
9	1	0	1259	-1121
		2	459	-411
		3	2904	-2609
		4	690	602
		5	988	832
		6	1513	1307
		7	106	-106
		8	463	446
10	1	0	740	724
		2	1982	1861
		3	1738	-1596
		4	218	-102
		5	301	283
		6	99	109

Upper section — group 3

h	k	l	100 F_o	100 F_c
		7	228	-218
		8	804	780
11	1	0	1388	1244
		2	284	-179
		3	235	157
		4	439	386
		5	281	185
		6	294	271
		7	<71	67
12	1	0	281	223
		2	205	-180
		3	274	-252
		4	763	-704
		5	73	-60
		6	195	175
13	1	0	136	111
		2	449	401
		3	<101	2
		4	406	-366
14	1	0	198	-89
		2	195	-172
11	1	3	181	185
		10	472	493
		9	303	-260
		8	474	402
		7	1589	-1510
		6	1394	-1326
		5	413	-353
		4	312	263
		3	775	651
		2	168	-175
		1	172	-126
		0	1201	1186
		-1	181	-36
		-2	282	325
		-3	674	624
		-4	607	-631
		-5	1506	-1379
		-6	683	-599
		-7	<108	16
		-8	726	704
		-9	<129	-66
		-10	1136	-1176
11	2	3	229	-212
		10	142	-139
		9	457	-401
		8	805	691
		7	1111	-1026
		6	<134	-76
		5	557	533

Upper section — group 4

h	k	l	100 F_o	100 F_c
		4	<119	-97
		3	187	136
		2	1102	985
		1	1291	-1243
		0	729	617
		-1	1222	1119
		-2	1763	-1639
		-3	2257	-1993
		-4	3204	-3292
		-5	1056	-985
		-6	857	-719
		-7	503	471
		-8	518	493
		-9	264	230
		-10	1831	1799
		-11	2262	2375
10	3	3	172	-173
		9	212	-226
		8	742	-735
		7	808	-716
		6	254	-185
		5	397	271
		4	1690	960
		3	855	786
		2	1109	-995
		1	1319	1221
		0	285	274
		-1	582	-529
		-2	215	110
		-3	1330	1172
		-4	1118	-1094
		-5	973	-824
		-6	1705	1698
		-7	460	391
		-8	1350	1359
		-9	134	164
		-10	1645	-1781
		-11	362	428
10	4	3	282	-201
		9	637	605
		8	120	151
		7	246	215
		6	1856	-1905
		5	1636	1634
		4	<132	89
		3	226	163
		2	<119	34
		1	1259	-1191
		0	687	912
		-1	196	-45

Lower section — group 1

h	k	l	100 F_o	100 F_c
		-2	3219	3591
		-3	944	-905
		-4	<110	-83
		-5	1270	1111
		-6	<122	-140
		-7	1039	1047
		-8	257	289
		-9	809	-832
		-10	601	-535
		-11	607	-544
		-12	1417	-1380
8	5	3	364	398
		7	607	668
		6	386	410
		5	1442	1512
		4	1028	975
		3	<132	-94
		2	802	752
		1	800	-810
		0	1019	-1024
		-1	2885	-3143
		-2	358	-341
		-3	190	208
		-4	1186	-1208
		-5	180	-52
		-6	445	-386
		-7	416	460
		-8	520	513
		-9	632	-708
		-10	<132	31
		-11	248	-245
9	6	3	328	-382
		8	1996	1784
		7	1534	-1632
		6	212	150
		5	656	652
		4	252	293
		3	348	-316
		2	1105	-1042
		1	212	169
		0	1625	-1598
		-1	1380	1373
		-2	<131	-98
		-3	1644	-1660
		-4	1136	-1166
		-5	<135	-9
		-6	137	122
		-7	806	765
		-8	423	379
		-9	<128	-128

Lower section — group 2

h	k	l	100 F_o	100 F_c
		-10	468	372
		-11	434	419
8	7	3	227	287
		7	1255	-1175
		6	<107	21
		5	475	-537
		4	1240	-1288
		3	238	-243
		2	827	-80
		1	<137	-2
		0	690	-723
		-1	736	729
		-2	1797	1913
		-3	2951	3222
		-4	723	721
		-5	<135	10
		-6	148	118
		-7	431	379
		-8	<123	-72
		-9	539	-557
		-10	194	-214
6	8	3	646	-586
		5	<96	88
		4	196	215
		3	236	-217
		2	338	331
		1	128	131
		0	291	318
		-1	245	220
		-2	892	895
		-3	358	-380
		-4	129	-131
		-5	584	566
		-6	373	380
		-7	579	-584
		-8	<103	-23
		-9	163	-165
3	9	3	291	313
		2	453	462
		1	<107	-73
		0	223	235
		-1	1437	-1470
		-2	1126	1245
		-3	891	-972
		-4	1026	-1100
		-5	1247	-1299
		-6	794	-767
		-7	324	283
		-8	751	-765
1	10	3	390	406

Lower section — group 3

h	k	l	100 F_o	100 F_c
0			650	-684
-1			171	48
-2			877	808
-3			621	-651
-4			542	-550
-5			508	520
0	0	2	221	-232
		4	1264	-1219
		6	719	-657
1	0	7	945	-840
		-5	199	-199
		-3	8108	6265
		-1	1854	-1690
		1	4328	-3947
		3	2257	-2280
		5	986	-869
		7	<194	-0
2	0	6	722	-805
		-4	1436	-1161
		-2	2772	-2712
		0	1647	1778
		2	1623	-1577
		4	1264	-1194
		6	689	-697
3	0	7	802	710
		-5	647	-606
		-3	1538	1548
		-1	3018	2991
		1	2762	-2869
		3	2240	-2327
		5	329	-308
4	0	6	1217	-1291
		-4	814	797
		-2	913	-917
		0	811	-792
		2	846	827
		4	884	887
		6	2458	2258
5	0	7	602	-639
		-5	448	-455
		-3	523	493
		-1	3026	2966
		1	<234	-61
		3	1354	1326
		5	1913	-1857
6	0	6	741	-805
		-4	729	677
		-2	2529	2203
		0	2110	-2188
		2	2559	-2515

Lower section — group 4

h	k	l	100 F_o	100 F_c
		4	<321	69
7	0	7	652	-661
		-5	2692	2812
		-3	318	-321
		-1	4058	3892
		1	344	-376
		3	269	253
		5	234	-204
8	0	6	<301	62
		-4	4067	3870
		-2	<286	97
		0	3544	-3612
		2	1027	-1116
		4	515	566
9	0	7	389	422
		-5	201	-204
		-3	3670	-3615
		-1	1090	-1111
		1	610	-593
		3	535	508
10	0	6	886	-900
		-4	695	724
		-2	<328	-133
		0	<67	-81
		2	328	-304
		4	<114	102
11	0	5	919	939
		-3	<328	12
		-1	762	-830
		1	881	899
		3	602	654
12	0	6	793	754
		-4	359	-349
		-2	824	869
		0	172	138
		2	1291	1512
13	0	5	<201	60
		-3	308	-323
		-1	95	-104
		1	1336	-1615
14	0	4	617	-612
		-2	1070	-1017
		0	468	-496

0·36; $|U_{020}| = 0·05$; now both signs of U_{800} satisfy the inequality, though with different margins.

According to the $(hk0)$ projection the long molecular axis of the molecule near $(0, 0)$ lies roughly parallel to either [111] or [$\bar{1}\bar{1}1$]. Approximate z coordinates for both orientations were derived from packing considerations and tested by structure-factor calculations; of the two models the former was found to correspond to the correct orientation.

Refinement

Details of our refinement procedure have been given in a previous publication (Coppens & Schmidt, 1964). The scattering factors employed were those given by Hoerni & Ibers (1954) for C, by Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for N and O, and by McWeeny (1952) for H. Unobserved reflections were assigned a threshold value F_t based on the lowest intensity readings and only included in the refinement when $|F_c| > kF_t$. The three levels were first refined separately, initially with isotropic, later with anisotropic temperature parameters of all but the hydrogen atoms. When these refinements had been completed the levels were merged, and the residuals used to estimate the relative accuracy of the levels (Coppens & Schmidt, 1964). Numerical details are given in Table 2.

Refinement of all data was continued until the shifts in positional and thermal parameters were random and less than a fifth of the estimated standard deviations of these parameters. 360 reflections (358 observed reflections + 2 unobserved reflections

with $|F_c| > kF_t$) were used to determine 113 parameters (3 scale factors, 45 positional and 65 thermal parameters).

Observed and calculated structure factors are listed in Table 3; final coordinates and temperature factors are given in Tables 4 and 5.

Table 5. *Temperature factors**

	β_{11}	β_{22}	β_{33}	β_{12}	β_{23}	β_{13}
O(1)	0·0052	0·0070	0·0132	−0·0029	−0·0031	0·0087
O(2)	0·0044	0·0058	0·0192	−0·0033	−0·0070	0·0061
O(3)	0·0044	0·0054	0·0199	−0·0008	0·0008	0·0097
N	0·0033	0·0044	0·0135	−0·0008	−0·0023	0·0042
C(1)	0·0031	0·0040	0·0115	0·0002	−0·0011	0·0035
C(2)	0·0036	0·0045	0·0098	0·0009	−0·0010	0·0030
C(3)	0·0040	0·0047	0·0137	−0·0006	−0·0001	0·0021
C(4)	0·0037	0·0044	0·0144	0·0003	0·0025	0·0058
C(5)	0·0039	0·0052	0·0087	0·0020	−0·0000	0·0037
C(6)	0·0035	0·0042	0·0134	0·0005	0·0022	0·0014

	B
H(O)	3·1
H(2)	−0·6
H(3)	−1·3
H(5)	−0·6
H(6)	0·4

* The temperature factors β and B are respectively the coefficients in the expressions $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{23}kl + \beta_{13}hl)]$ and $\exp[-(B\sin^2\theta/\lambda^2)]$.

Table 4. *Final fractional coordinates of α-p-nitrophenol*

Heavy atoms*

Atom	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
O(1)	−0·0586	0·2931	0·8930	0·0003	0·0004	0·0006
O(2)	−0·0864	0·1267	0·6215	0·0003	0·0004	0·0006
O(3)	0·3188	0·5238	0·4370	0·0003	0·0004	0·0006
N	−0·0350	0·2409	0·7240	0·0003	0·0005	0·0007
C(1)	0·0554	0·3144	0·6431	0·0003	0·0005	0·0008
C(2)	0·1138	0·4413	0·7612	0·0003	0·0005	0·0007
C(3)	0·2013	0·5104	0·6860	0·0004	0·0005	0·0008
C(4)	0·2298	0·4526	0·4971	0·0004	0·0005	0·0008
C(5)	0·1689	0·3267	0·3777	0·0003	0·0005	0·0007
C(6)	0·0800	0·2580	0·4503	0·0003	0·0005	0·0009

Hydrogen atoms*

Atom	Observed			Calculated†		
H(O)	0·3354	0·4891	0·3614	0·3524	0·4704	0·3250
H(2)	0·0934	0·4851	0·8816	0·0911	0·4849	0·9089
H(3)	0·2413	0·6095	0·7768	0·2478	0·6097	0·7742
H(5)	0·1868	0·2924	0·2487	0·1911	0·2832	0·2295
H(6)	0·0434	0·1597	0·3674	0·0305	0·1618	0·3581

* For the numbering of the heavy atoms see Figs. 2 and 3. H(O) is the hydroxylic hydrogen; H(n) is the hydrogen atom bonded to C(n).

† Calculated assuming the aromatic HC = 1·08 Å, bisecting the angle between the adjacent C–C bonds, and the hydroxylic hydrogen at 1·00 Å from O(3) towards the acceptor atom O(2).
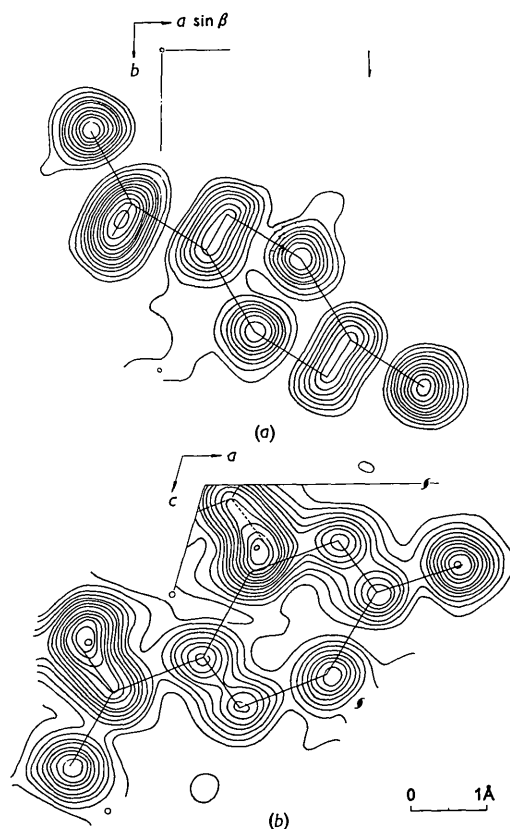

Fig. 1. Electron density projections. Contours each 1 e.Å^{-2}, lowest contour at 2 e.Å^{-2}. (a) Projection along [001]. (b) Projection along [010].

Final overall agreement factors are

$$r = \Sigma w(k^2 F_o^2 - F_c^2)^2 / \Sigma w k^4 F_o^4 = 3.5\%$$

and

$$R = \Sigma(|kF_o - |F_c||) / \Sigma kF_o = 8.3\% \ .$$

For 6 reflections $2|F_c| < kF_o$, while for 2 out of the total 35 unobserved reflections $F_c > kF_t$. Electron density projections and packing diagrams along [001] and [010] are shown in Figs. 1 and 2.
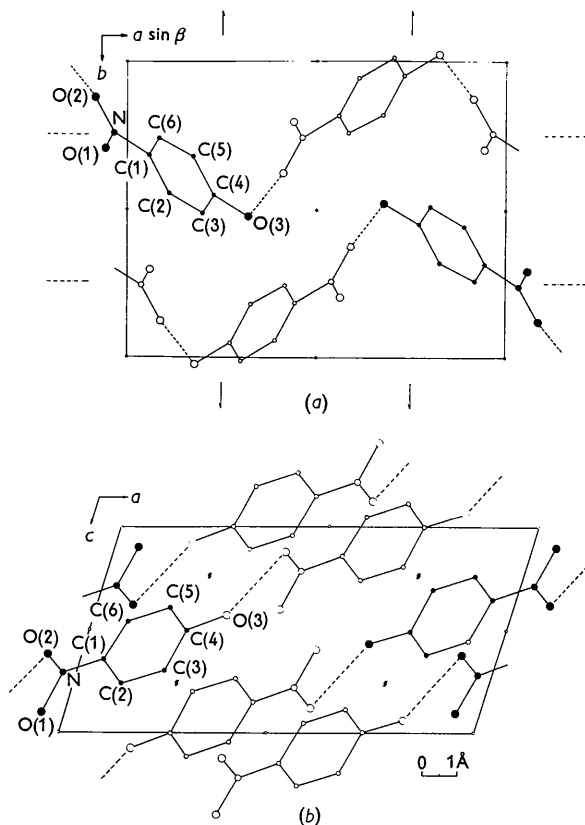

Fig. 2. Packing diagrams,
(a) seen along [001], (b) seen along [010].

Discussion

Packing arrangement

The structure contains infinite chains of glide-plane related molecules linked together by hydrogen bonds. The angle between the benzene-ring planes of adjacent molecules in a chain is 74°.

Every molecule is faced by a second one at a distance of 3.33 Å and related to it by a center of symmetry. Additional van der Waals contacts are made with twelve other molecules. Eleven of these are listed in Table 6; the two others are at $x, y, z-1$ and $\frac{1}{2}+x, \frac{1}{2}-y, z+\frac{1}{2}$. Distances to these two molecules are identical with those to molecules I and III given in Table 6. The molecule at $\bar{x}, \bar{y}, \bar{z}$ is at a somewhat larger distance, the shortest interatomic vector to it being 3.96 Å (O(2)–O(2)).

Molecular structure

The benzene ring is planar, but the nitro group and the hydroxylic oxygen atom are displaced from the plane of the ring (Table 7). Such deviations from planarity are quite common in substituted aromatic molecules, as for example in benzoic acid (Sim,

Table 6. Intermolecular distances (Å)

Distances are given between reference molecule of which the atomic coordinates are listed in Table 4 and surrounding molecules

Distances involving hydrogen atoms are based on calculated hydrogen coordinates given in Table 4

(I)	$x, y, 1+z$	(VII)	$\bar{x}, 1-y, 1-z$
(II)	$x-\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}+z$	(VIII)	$\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$
(III)	$x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$	(IX)	$\frac{1}{2}-x, \frac{1}{2}+y, 1\frac{1}{2}-z$
(IV)	$\frac{1}{2}+x, \frac{1}{2}-y, z-\frac{1}{2}$	(X)	$\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$
(V)	$\bar{x}, \bar{y}, 1-z$	(XI)	$\frac{1}{2}-x, y-\frac{1}{2}, 1\frac{1}{2}-z$
(VI)	$\bar{x}, 1-y, 2-z$		

Distances between heavy atoms: (<3.5 Å)		Distances involving hydrogen atoms: (<3 Å)	
O(1)C(5)(I)	3.33	O(1)H(6)(I)	2.95
O(1)C(6)(I)	3.31	H(2)H(5)(I)	2.63
O(1)C(4)(II)	3.47	O(2)H(O)(II)	1.82*
O(1)C(5)(II)	3.31	O(2)H(5)(II)	2.96
O(2)C(3)(III)	3.26	O(1)H(5)(II)	2.86
O(3)O(1)(IV)	3.17	O(1)H(O)(II)	2.52
O(3)O(2)(IV)	2.82*	NH(O)(II)	2.45
O(2)C(6)(V)	3.41	O(2)H(6)(V)	2.61
O(1)C(2)(VI)	3.33	O(1)H(2)(VI)	2.38
O(3)O(1)(VII)	3.48	H(2)H(2)(VI)	2.69
O(1)C(4)(VII)	3.43	O(3)H(5)(VIII)	2.48
NC(3)(VII)	3.44	H(3)H(6)(IX)	2.90
C(2)C(1)(VII)	3.41	H(5)H(O)(X)	2.79
C(3)C(1)(VII)	3.42	H(6)H(O)(X)	2.62
C(6)C(2)(VII)	3.46	C(6)H(3)(XI)	2.55
O(3)C(5)(VIII)	3.31	C(5)H(3)(XI)	2.80
O(3)N(IX)	3.33	C(1)H(3)(XI)	2.83

* Hydrogen bond.

Table 7

Equations of planes

Benzene-ring: $6.2340x - 5.2864y + 2.4667z - 0.2570 = 0$
Nitro-group: $6.4154x - 5.1074y + 2.4734z - 0.3358 = 0$

Angle between the two planes: 1° 32′

The benzene ring plane is derived according to Schomaker, Waser, Marsh & Bergman (1959)

Out-of-plane displacements

Atom	From benzene ring	Atom	From benzene ring
O(1)	0.031 Å	H(2)	−0.06 Å
O(2)	0.068	H(3)	−0.06
O(3)	0.039	H(5)	−0.02
N	0.037	H(6)	0.07
C(1)	0.013		From NO$_2$
C(2)	−0.003	C(1)	0.013
C(3)	−0.008		
C(4)	0.009		
C(5)	0.001		
C(6)	−0.011		

Robertson & Goodwin, 1955), p-dinitrobenzene (Abrahams, 1950), m-dinitrobenzene (Trotter, 1961) and nicotinic acid (Wright & King, 1953). Larger deviations from planarity are observed in the other modification of p-nitrophenol (Coppens & Schmidt, 1965).

The intramolecular distances and angles are shown in Fig. 3. The average standard deviation in the bond lengths is 0·006 Å, while the average standard deviation in the angles is 0·4°. The distances between the heavy atoms are all compatible with values recorded in the literature, and equal within the experimental errors with corresponding distances in the β form of p-nitrophenol. We shall discuss these dimensions in the paper on the structure of the β modification.

Hydrogen temperature factors

The fact that three out of five hydrogen 'temperature factors' are negative (Table 5) deserves some comment. The errors in these parameters are very large, but the negative sign indicates that the electron density is more concentrated in the bonded atom than in the free atom from which the f curve is derived. This is in agreement with recent calculations of the scattering factor of a hydrogen atom in a hydrogen molecule (Iijima & Bonham, 1963). Negative temperature factors for the hydrogen atoms have been observed in other low-temperature structures (e.g. Hirshfeld, Sandler & Schmidt, 1963).

Fig. 3. Bond lengths and angles. Average standard deviation in bond lengths 0·006 Å, in angles 0·4°.

References

ABRAHAMS, S. C. (1950). Acta Cryst. 3, 194.
BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOP-STRA, B. O., MacGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). Acta Cryst. 8, 478.
COPPENS, P., SCHMIDT, G. M. J. & GILLIS, J. (1958). Proc. Kon. Ned. Akad. Wetenschappen, B 61, 196.
COPPENS, P. & SCHMIDT, G. M. J. (1964). Acta Cryst. 17, 222.
COPPENS, P. & SCHMIDT, G. M. J. (1965). Acta Cryst. In the press.
FRITZSCHE, J. (1859). Liebigs Ann. 110, 157.
GILLIS, J. (1948). Acta Cryst. 1, 174.
HARKER, D. & KASPER J. S. (1948). Acta Cryst. 1, 70.
HIRSHFELD, F. L., SANDLER, S. & SCHMIDT, G. M. J. (1963). J. Chem. Soc. p. 2108.
HIRSHFELD, F. L. & SCHMIDT, G. M. J. (1956). Acta Cryst. 9, 233.
HOERNI, J. A. & IBERS, J. A. (1954). Acta Cryst. 7, 744.
IIJIMA, T. & BONHAM, R. A. (1963). Acta Cryst. 16, 1061.
McWEENY, R. (1952). Acta Cryst. 5, 463.
SCHMIDT, G. M. J. (1957). Acta Cryst. 10, 793.
SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). Acta Cryst. 12, 600.
SIM, G. A., ROBERTSON, J. M. & GOODWIN, T. H. (1955). Acta Cryst. 8, 157.
TOUSSAINT, J. (1954). Bull. Soc. Sci. Liège, 23, 24.
TROTTER, J. (1961). Acta Cryst. 14, 244.
WILSON, A. J. C. (1942). Nature, Lond. 150, 152.
WRIGHT, W. B. & KING, G. S. D. (1953). Acta Cryst. 6, 305.