The intramolecular distances from the six hydrogen atoms of the methyl groups to the nearest hydrogen atoms of the aromatic nucleus were calculated to vary between 2·29 and 2·34 Å, thus being only slightly shorter than the mutual distances of neighbouring aromatic hydrogen atoms, which were calculated to vary between 2·48 and 2·50 Å.

It is concluded that the slightly distorted shape of the molecule found by this crystal structure analysis is consistent with our knowledge about the shortest possible intramolecular distances between hydrogen atoms.

Finally the shortest interatomic distances between one molecule and its neighbours have been computed. Nine of the distances between carbon atoms of a molecule and hydrogen atoms of neighbouring molecules are shorter than 3 Å, the shortest being 2·86 Å. Each molecule moreover has 37 intermolecular H–H distances representing 19 crystallographically independent distances that are smaller than 3 Å, the shortest being 2·49 Å. The shortest intermolecular distances in

anthracene (Cruickshank, 1956) and naphthalene (Cruickshank, 1957) are for C–H 2·67 and 2·82 Å and for H–H 2·50 and 2·40 Å, respectively. The intermolecular distances calculated in this investigation, therefore, agree well with those found in similar compounds.

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# The Crystal Structure of the Metastable (β) Modification of *p*-Nitrophenol

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The crystal structure of the β modification of *p*-nitrophenol has been refined from three-dimensional counter data to an *R* value of 6·9%. Bond lengths have been determined with an e.s.d. of better than 0·003 Å, and corrected for thermal motion, the analysis of which suggests that the molecule as a whole does not behave as a rigid body. The packing arrangements of this modification and of the previously determined α form are compared; an explanation for the thermodynamic relationship of the two forms is given in terms of molecular close-packing. The photochemical behaviour of the two forms is tentatively explained in terms of the geometry of the intermolecular C–H · · · O–N contacts.

### Introduction

*p*-Nitrophenol undergoes a photochemical reaction in the solid state (Fritzsche, 1859) whose detailed chemical mechanism is not known but which we assume to involve in its initial stage the redox reaction

$$-NO_2 + \, > CH \xrightarrow{h\nu} -NO + \, > C(OH) \qquad (1)$$
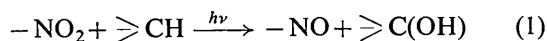
The reaction, which manifests itself in the irreversible color change of the solid from yellow to red, is topochemically controlled (Cohen & Schmidt, 1964) since it is confined to the solid state and, more specifically, to one of the two known crystalline modifications.

In order to analyze the geometric factors controlling the intermolecular redox step we have undertaken in parallel with our investigation of the *o*-nitrobenzalde-

hydes (Coppens & Schmidt, 1964) in which the redox reaction (1) takes place intramolecularly, the structure analysis of the photoactive (α) modification of *p*-nitrophenol (Coppens & Schmidt, 1965); its packing arrangement was to be compared with that of the light-stable (β) form published by Toussaint (1954). A first comparison of the two structures showed a large difference in the OH · · · O distances: α: 2·82 Å (at 90 °K), β: 2·65 Å, which on the basis of Toussaint's estimate of a mean error of 0·04 Å would be significant. However, our measurements of the infrared spectrum of powdered β-nitrophenol gave the OH stretching frequency at about 3250 cm⁻¹, very close to the corresponding band in the α form. Since an OH · · · O distance of 2·65 Å would require this band to lie near 2750 cm⁻¹ (Nakamoto, Margoshes & Rundle, 1955)

it seemed likely that the published coordinates of the $\beta$ form were not accurate enough for our purpose; it was therefore decided to refine the structure.

## Experimental

Needle-shaped crystals elongated along [001] were obtained by slow evaporation of an aqueous solution. Such crystals could be cut with a razor blade; a specimen with dimensions $0.3 \times 0.4 \times 0.4$ mm was chosen for data collection. Cell dimensions at 90 °K (determined from Weissenberg photographs and corrected for film shrinkage), and at room temperature (measured on the General Electric spectrogoniometer) are listed in Table 1.

Table 1. *Crystallographic constants of $\beta$-p-nitrophenol*

| | At room temperature | | Near 90 °K |
|---|---|---|---|
| | Toussaint 1954 | Our measurements | |
| $a$ | 15·4 Å | 15·403 ± 0·003 Å | 15·21 ± 0·02 Å |
| $b$ | 11·2 | 11·117 ± 0·002 | 11·04 ± 0·02 |
| $c$ | 3·8 | 3·785 ± 0·001 | 3·622 ± 0·006 |
| $\beta$ | 106°55′ | 107°4′ ± 2′ | 106°49′ ± 10′ |
| $D_x(n=4)$ | | 1·491 g.cm⁻³ | 1·570 g.cm⁻³ |
| Space group | $P2_1/a$ | | $P2_1/a$ |

Intensities of the accessible reflections (1373 in all) and the background in their neighborhood were measured on a G.E. spectrogoniometer with Ni-filtered Cu $K$ radiation by means of the stationary-crystal, stationary-counter technique (Furnas, 1957). All intensities were counted for ten seconds; strong intensities were measured with an attenuator, inserted between the target and the crystal in order to eliminate dead-time losses in the SPG 1 proportional counter. The strongest reflection corresponded to 70,000 counts sec⁻¹, background on the average to 3 counts sec⁻¹. Up to $2\theta = 120°$ the $\alpha_1$ and $\alpha_2$ reflections were counted together. At this angle the total width of the doublet becomes larger than the counter aperture; since the two components were properly resolved for $2\theta > 120°$ it was possible to measure $\alpha_1$ separately in this range. The total intensity of the doublet was subsequently obtained by a 50% scale up of the observed intensity.

The measured intensities were qualitatively compared with Weissenberg-film data; four errors, due to incorrect setting of the goniometer circles, were eliminated by remeasurement of these reflections. An additional four reflections had to be excluded from the final least-squares cycles because of abnormally high discrepancies between $F_o$ and $F_c$, which we attribute to observational errors.

## Data reduction and refinement

Weights were based on the statistical counting error in the 10 seconds' count and on a proportional error, represented respectively by the first and the second term in the expression

$$\sigma^2(I-B) = \frac{I+B+2}{10} + c^2(I-B)^2$$

in which $I$ and $B$ are, respectively, the intensity and the background in counts per sec; the two in the numerator of the first term represents a round-off error (introduced by the invisibility of the last decade of the scaler). The constant $c$ was estimated to be 0·03 from a comparison of the intensities of symmetry-related reflections. Whenever $I$ and $B$ differed by less than one standard deviation the reflection was considered unobserved, and a threshold value $F_t$ derived from $\sigma(I-B)$. (These unobserved reflections are included in the refinement only when $|F_c| > kF_t$).

Refinement was carried out with a diagonal-matrix least-squares program written by Dr. F. L. Hirshfeld of this Department for WEIZAC. This program minimizes the function

$$r = \frac{\Sigma w(k^2 F_o^2 - F_c^2)^2}{\Sigma w k^4 F_o^4}$$

with respect to the scale factor $k$ and the positional and thermal parameters of each atom in the asymmetric unit. 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.

Toussaint's coordinates (Toussaint, 1954) were used as input for the first least-squares cycle, which included only $hk0$ reflections; after a few cycles anisotropic temperature factors were introduced, while hydrogen atoms were added and refined isotropically. Higher levels were gradually included as refinement proceeded. In the course of the refinement the molecule rotated around the line C(2)–C(5) (for numbering of the atoms see Fig. 2). The changes in $z$ coordinates ranged up to 0·19 Å for O(2), while the $x$ and $y$ coordinates changed relatively little.

When the structure had converged to $r=2.96\%$ the list of calculated and observed structure factors was examined for extinction. For the 88 strongest reflections $\ln(I_c/I_o)$ was plotted against $I_c$. A least-squares line was fitted to all but the three strongest reflections which were obviously quite far below the line. This is not unexpected as the one-parameter function used here is not valid for strong extinction [see Hamilton (1957): for these three reflections $\sigma D > 1$]. When $I_c$ was put on the absolute scale established by the least-squares refinement the slope of the line was found to be $5.92 \times 10^{-4}$. Subsequently $F_o$ of 83 reflections were multiplied by $\exp(2.96 \times 10^{-4} I_c)$; the three strongest reflections were excluded from the refinement. For all other reflections the correction amounts to less than 1% of $F_o$. We also investigated whether extinction increased as the scattering angle approached 45° (Zachariasen, 1963): no angle dependency could be detected, mainly because only the strong low-order reflections were appreciably affected by extinction.

Table 2. *Observed and calculated structure factors*

Sign < indicates unobserved reflection; 7 reflections marked with asterisks were excluded from final least-squares cycles. One asterisk: because of extinction: two asterisks: because of experimental error.

| h | k | l | 200 $F_o$ | 200 $F_c$ |
|---|---|---|---|---|
| 0 | 2 | 0 | 7841 | -7467 |
|  | 4 |  | 6485 | 6575 |
|  | 6 |  | 364 | -46 |
|  | 8 |  | 1698 | -1538 |
|  | 10 |  | 1078 | -925 |
|  | 12 |  | 706 | 669 |
|  | 14 |  | 364 | -421 |
| 1 | 1 | 0 | 2202 | -2400 |
|  | 2 |  | 9366 | 10137 |
|  | 3 |  | 1869 | 2005 |
|  | 4 |  | 5688 | 5886 |
|  | 5 |  | 3273 | -3146 |
|  | 6 |  | 4816 | 4676 |
|  | 7 |  | 2927 | 2735 |
|  | 8 |  | 314 | 260 |
|  | 9 |  | 382 | -309 |
|  | 10 |  | 519 | 466 |
|  | 11 |  | 970 | -1014 |
|  | 12 |  | 963 | 1036 |
|  | 13 |  | 173 | 157 |
|  | 14 |  | 123 | 103 |
| 2 | 0 | 0 | 1417 | 1387 |
|  | 1 |  | 4939 | -4970 |
|  | 2 |  | 6546* | -10605 |
|  | 3 |  | 3522 | 3794 |
|  | 4 |  | 3958 | -3854 |
|  | 5 |  | 2184 | -2242 |
|  | 6 |  | 4048 | 3877 |
|  | 7 |  | 1763 | 1845 |
|  | 8 |  | 616 | -665 |
|  | 9 |  | 372 | 389 |
|  | 10 |  | 1517 | -1562 |
|  | 11 |  | 317 | 338 |
|  | 12 |  | 826 | 860 |
|  | 14 |  | 75 | -98 |
| 3 | 1 | 0 | 130 | -91 |
|  | 2 |  | 1637 | -1642 |
|  | 3 |  | 1053 | -882 |
|  | 4 |  | 2186 | 2183 |
|  | 5 |  | 1334 | -1400 |
|  | 6 |  | 285 | 222 |
|  | 7 |  | 1965** | 2700 |
|  | 8 |  | 1143 | 1166 |
|  | 9 |  | 764 | -739 |
|  | 10 |  | 1161 | -1235 |
|  | 11 |  | 955 | 1021 |
|  | 12 |  | 368 | -393 |
|  | 13 |  | 100 | 85 |
|  | 14 |  | 760 | -664 |
| 4 | 0 | 0 | 6237 | 6529 |
|  | 1 |  | 3252 | 3572 |
|  | 2 |  | 7538 | -8316 |
|  | 3 |  | 4564 | -4536 |
|  | 4 |  | 1770 | -1630 |
|  | 5 |  | 2657 | -2746 |
|  | 6 |  | 584 | 582 |
|  | 7 |  | 227 | 103 |
|  | 8 |  | 1698 | 1691 |
|  | 9 |  | 1078 | 959 |
|  | 10 |  | 616 | 640 |
|  | 11 |  | 137 | -33 |
|  | 12 |  | 458 | 446 |
|  | 13 |  | 706 | 639 |
| 5 | 1 | 0 | 3919 | 3917 |
|  | 2 |  | 173 | -65 |
|  | 3 |  | 4485 | -4433 |
|  | 4 |  | 3873 | -2780 |
|  | 5 |  | 1146 | -1224 |
|  | 6 |  | 1467 | -1354 |
|  | 7 |  | 386 | -431 |
|  | 8 |  | 3461 | -357 |
|  | 9 |  | 2160 | -2204 |
|  | 10 |  | 490 | 445 |
|  | 11 |  | 627 | 581 |
|  | 12 |  | 429 | -380 |
|  | 13 |  | 37 | -71 |
| 6 | 0 | 0 | 4225 | 4391 |
|  | 1 |  | 5469 | 5864 |
|  | 2 |  | 634 | 320 |
|  | 3 |  | 497 | 540 |
|  | 4 |  | 4192 | 4375 |
|  | 5 |  | 2397 | -2486 |
|  | 6 |  | 411 | 490 |
|  | 7 |  | 934 | 974 |
|  | 8 |  | 2729 | 2792 |
|  | 9 |  | 1712 | -1796 |
|  | 10 |  | 3057 | -3054 |
|  | 11 |  | 1024 | -1193 |
|  | 12 |  | 209 | 205 |
|  | 13 |  | <69 | -31 |
| 7 | 1 | 0 | 4838 | 5596 |
|  | 2 |  | 4625 | -4596 |
|  | 3 |  | 1875 | -2060 |
|  | 4 |  | 2509 | 2848 |
|  | 5 |  | 2920 | 3335 |
|  | 6 |  | 544 | -632 |
|  | 7 |  | 724 | 803 |
|  | 8 |  | 2632 | 3239 |
|  | 9 |  | 649 | -732 |
|  | 10 |  | 1143 | 1329 |
|  | 11 |  | 317 | -345 |
|  | 12 |  | 382 | 321 |
|  | 13 |  | 130 | -87 |
| 8 | 0 | 0 | 3922 | 3874 |
|  | 1 |  | 3100 | 3196 |
|  | 2 |  | 3317 | -3336 |
|  | 3 |  | 2491 | 2440 |
|  | 4 |  | 1543 | -1267 |
|  | 5 |  | 901 | -893 |
|  | 6 |  | 2899 | -2973 |
|  | 7 |  | 4218 | 4347 |
|  | 8 |  | 130 | 56 |
|  | 9 |  | 829 | -821 |
|  | 10 |  | 263 | -198 |
|  | 11 |  | 440 | 427 |
|  | 12 |  | 242 | 271 |
| 9 | 1 | 0 | 1409 | -1358 |
|  | 2 |  | 891 | 873 |
|  | 3 |  | 2845 | -2940 |
|  | 4 |  | 952 | 840 |
|  | 5 |  | 934 | -967 |
|  | 6 |  | 494 | -492 |
|  | 7 |  | 2498 | 2545 |
|  | 8 |  | 1060 | -963 |
|  | 9 |  | 515 | -466 |
|  | 10 |  | 144 | -163 |
|  | 11 |  | 1136 | 1061 |
|  | 12 |  | 544 | -481 |
| 10 | 0 | 0 | 688 | -636 |
|  | 1 |  | 1013 | 1049 |
|  | 2 |  | 310 | 331 |
|  | 3 |  | 252 | -231 |
|  | 4 |  | <87 | 7 |
|  | 5 |  | 1780 | -1781 |
|  | 6 |  | 461 | 506 |
|  | 7 |  | 94 | 107 |
|  | 8 |  | 364 | 332 |
|  | 9 |  | 310 | -324 |
|  | 10 |  | 332 | -333 |
|  | 11 |  | <61 | -0 |
|  | 12 |  | 309 | 381 |
| 11 | 1 | 0 | 479 | -429 |
|  | 2 |  | <87 | 131 |
|  | 3 |  | 1409 | -1353 |
|  | 4 |  | 1099 | -1130 |
|  | 5 |  | 364 | 284 |
|  | 6 |  | 200 | -195 |
|  | 7 |  | 869 | 884 |
|  | 8 |  | 397 | 396 |
|  | 9 |  | 590 | -530 |
|  | 10 |  | 429 | -356 |
|  | 11 |  | 523 | -472 |
| 12 | 0 | 0 | 3356 | 3377 |
|  | 1 |  | 862 | -722 |
|  | 2 |  | 1363 | -1258 |
|  | 3 |  | 1705 | -1744 |
|  | 4 |  | 1136 | 1192 |
|  | 5 |  | 1146 | -1146 |
|  | 6 |  | 1193 | -1258 |
|  | 7 |  | 674 | -653 |
|  | 8 |  | 541 | 505 |
|  | 9 |  | 415 | 375 |
|  | 10 |  | 184 | -141 |
|  | 11 |  | 159 | -182 |
| 13 | 1 | 0 | 2974 | 2905 |
|  | 2 |  | 2823 | 2829 |
|  | 3 |  | 418 | 541 |
|  | 4 |  | 1078 | -993 |
|  | 5 |  | <87 | -166 |
|  | 6 |  | 1113 | 1193 |
|  | 7 |  | 234 | 201 |
|  | 8 |  | 184 | -164 |
|  | 9 |  | 613 | -658 |
|  | 10 |  | 469 | -424 |
| 14 | 0 | 0 | 1272 | -1278 |
|  | 1 |  | 1648 | -1541 |
|  | 2 |  | 703 | -661 |
|  | 3 |  | 2682 | 2701 |
|  | 4 |  | 490 | 487 |
|  | 5 |  | 314 | 280 |
|  | 6 |  | <75 | -88 |
|  | 7 |  | 710 | 738 |
|  | 8 |  | 1053 | 1037 |
|  | 9 |  | 469 | 421 |
| 15 | 1 | 0 | 587 | -605 |
|  | 2 |  | 249 | 280 |
|  | 3 |  | 1457 | -1360 |
|  | 4 |  | 1182 | -1186 |
|  | 5 |  | 137 | 126 |
|  | 6 |  | <72 | -55 |
|  | 7 |  | 130 | -92 |
|  | 8 |  | 869 | 743 |
| 16 | 0 | 0 | 202 | 63 |
|  | 1 |  | 274 | -254 |
|  | 2 |  | <79 | 125 |
|  | 3 |  | <75 | -77 |
|  | 4 |  | 130 | -146 |
|  | 5 |  | <65 | -14 |
|  | 6 |  | 152 | -163 |
|  | 7 |  | 79 | -65 |
| 17 | 1 | 0 | 148 | 120 |
|  | 2 |  | 436 | 436 |
|  | 3 |  | 97 | -113 |
|  | 4 |  | 991 | -884 |
|  | 5 |  | 407 | -345 |
|  | 6 |  | <57 | -7 |
| 18 | 0 | 0 | 566 | 521 |
|  | 1 |  | 105 | 51 |
|  | 2 |  | 155 | -85 |
|  | 3 |  | 350 | 294 |
|  | 4 |  | 191 | 205 |
| -19 | 1 | 1 | 166 | 111 |
|  | 2 |  | 465 | 456 |
|  | 3 |  | 339 | -300 |
| -18 | 0 | 1 | <65 | 53 |
|  | 1 |  | 844 | -821 |
|  | 2 |  | <75 | -27 |
|  | 3 |  | <75 | -75 |
|  | 4 |  | 796 | 761 |
|  | 5 |  | 303 | -295 |
| -17 | 1 | 1 | <72 | 93 |
|  | 2 |  | 416 | -372 |
|  | 3 |  | 804 | 860 |
|  | 4 |  | 94 | 71 |
|  | 5 |  | 692 | -695 |
|  | 6 |  | 447 | 476 |
|  | 7 |  | <51 | 10 |
| -16 | 0 | 1 | 891 | 832 |
|  | 1 |  | 706 | -696 |
|  | 2 |  | <79 | 40 |
|  | 3 |  | 360 | 300 |
|  | 4 |  | 202 | -212 |
|  | 5 |  | 342 | 337 |
|  | 6 |  | 339 | 352 |
|  | 7 |  | 216 | 233 |
|  | 8 |  | 170 | 137 |
| -15 | 1 | 1 | 422 | 331 |
|  | 2 |  | 360 | -301 |
|  | 3 |  | 883 | 957 |
|  | 4 |  | 941 | 989 |
|  | 5 |  | 487 | -539 |
|  | 6 |  | 479 | 480 |
|  | 7 |  | 285 | -300 |
|  | 8 |  | 270 | -211 |
|  | 9 |  | 700 | 623 |
| -14 | 0 | 1 | 981 | 880 |
|  | 1 |  | 977 | 925 |
|  | 2 |  | 3554 | -3683 |
|  | 3 |  | 710 | 661 |
|  | 4 |  | 173 | 226 |
|  | 5 |  | 1071 | 1133 |
|  | 6 |  | 180 | -145 |
|  | 7 |  | 270 | 272 |
|  | 8 |  | <64 | 130 |
|  | 9 |  | 649 | -645 |
|  | 10 |  | 173 | -133 |
| -13 | 1 | 1 | 2704 | -2815 |
|  | 2 |  | 2747 | -2828 |
|  | 3 |  | 1427 | 1484 |
|  | 4 |  | 627 | -762 |
|  | 5 |  | 1427 | -1471 |
|  | 6 |  | 847 | -848 |
|  | 7 |  | 1197 | 1260 |
|  | 8 |  | 959 | -1011 |
|  | 9 |  | 265 | 237 |
|  | 10 |  | 170 | 172 |
| -12 | 0 | 1 | 5406 | 5717 |
|  | 1 |  | 3652 | -3781 |
|  | 2 |  | 443 | 106 |
|  | 3 |  | 564 | 602 |
|  | 4 |  | 636 | 582 |
|  | 5 |  | 1617 | -1934 |
|  | 6 |  | <83 | -142 |
|  | 7 |  | 350 | 359 |
|  | 8 |  | 746 | -757 |
|  | 9 |  | 461 | -474 |
|  | 10 |  | 130 | 84 |
|  | 11 |  | <65 | -57 |
| -11 | 1 | 1 | 927 | 846 |
|  | 2 |  | 609 | -416 |
|  | 3 |  | 1017 | 1053 |
|  | 4 |  | 1957 | 1932 |
|  | 5 |  | 559 | -650 |
|  | 6 |  | 686 | 660 |
|  | 7 |  | <83 | 49 |
|  | 8 |  | 1161 | -1144 |
|  | 9 |  | 415 | 334 |
|  | 10 |  | 97 | 110 |
|  | 11 |  | 371 | -274 |
| -10 | 0 | 1 | 209 | 200 |
|  | 1 |  | <72 | -70 |
|  | 2 |  | 303 | 311 |
|  | 3 |  | 580 | 485 |
|  | 4 |  | 162 | 34 |
|  | 5 |  | 533 | 510 |
|  | 6 |  | 285 | 338 |
|  | 7 |  | <83 | -21 |
|  | 8 |  | 483 | -473 |
|  | 9 |  | 339 | -356 |
|  | 10 |  | 804 | -773 |
|  | 11 |  | 736 | 673 |
|  | 12 |  | 360 | -349 |
| -9 | 1 | 1 | 688 | 649 |
|  | 2 |  | 1258 | -1491 |
|  | 3 |  | 461 | 417 |
|  | 4 |  | 3072 | 3063 |
|  | 5 |  | 638 | 578 |
|  | 6 |  | 2408 | 2450 |
|  | 7 |  | 1806 | 1764 |
|  | 8 |  | 930 | -923 |
|  | 9 |  | 959 | -994 |
|  | 10 |  | 746 | 715 |
|  | 11 |  | 541 | 524 |
|  | 12 |  | 772 | -799 |
| -8 | 0 | 1 | 2091 | -1918 |
|  | 1 |  | 2855 | -2845 |
|  | 2 |  | 3565 | -3617 |
|  | 3 |  | 494 | -342 |
|  | 4 |  | 422 | 337 |
|  | 5 |  | 267 | 197 |
|  | 6 |  | 1496 | -1527 |
|  | 7 |  | 1709 | 1703 |
|  | 8 |  | 2559 | 2596 |
|  | 9 |  | 1290 | 1252 |
|  | 10 |  | <83 | -38 |
|  | 11 |  | 530 | 571 |
|  | 12 |  | 443 | 427 |
|  | 13 |  | 569 | 583 |
| -7 | 1 | 1 | 1805 | 1806 |
|  | 2 |  | 4679 | -4791 |
|  | 3 |  | 8681 | -8448 |
|  | 4 |  | 1828 | 1750 |
|  | 5 |  | <83 | -24 |
|  | 6 |  | 1334 | -1246 |
|  | 7 |  | 2747 | -2760 |
|  | 8 |  | 2405 | -2370 |
|  | 9 |  | <97 | 43 |
|  | 10 |  | 609 | 545 |
|  | 11 |  | 605 | 606 |
|  | 12 |  | 104 | -159 |
|  | 13 |  | 664 | 646 |
| -6 | 0 | 1 | 1009 | -1057 |
|  | 1 |  | 674 | -760 |
|  | 2 |  | 1575 | 1377 |
|  | 3 |  | 1810 | 1756 |
|  | 4 |  | 2657 | 2543 |
|  | 5 |  | 2905 | -2772 |
|  | 6 |  | 591 | -584 |
|  | 7 |  | 465 | -416 |
|  | 8 |  | 2441 | 2493 |
|  | 9 |  | 4553 | -4599 |
|  | 10 |  | 1053 | -1085 |
|  | 11 |  | 458 | 474 |
|  | 12 |  | <72 | 147 |
|  | 13 |  | 670 | -664 |
| -5 | 1 | 1 | 4881 | 4857 |
|  | 2 |  | 8490 | -8251 |
|  | 3 |  | 970 | 810 |
|  | 4 |  | 2408 | 2249 |
|  | 5 |  | 2415 | 2473 |
|  | 6 |  | 1619 | -1651 |
|  | 7 |  | 2761 | 2828 |
|  | 8 |  | <90 | 126 |
|  | 9 |  | 2797 | -2829 |
|  | 10 |  | 1586 | 1507 |
|  | 11 |  | <87 | -57 |
|  | 12 |  | 353 | 359 |
|  | 13 |  | 764 | -730 |
| -4 | 0 | 1 | 2859 | 2951 |
|  | 1 |  | 5797 | -5847 |
|  | 2 |  | 2390 | 2286 |
|  | 3 |  | 3962 | 4037 |
|  | 4 |  | 1326 | -1192 |
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|  | 7 |  | 429 | 388 |
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|  | 7 |  | 451 | -439 |
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|  | 11 |  | 263 | 282 |
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| | 5 | | 260 | -274 |
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| | 4 | | 844 | -832 |
| | 5 | | 1197 | 1156 |
| | 6 | | 170 | -171 |
| | 7 | | 155 | -166 |
| | 8 | | <75 | -130 |
| | 9 | | 317 | 313 |
| 11 | 1 | 2 | 245 | 169 |
| | 2 | | 281 | 291 |
| | 3 | | 379 | -368 |
| | 4 | | 306 | -257 |
| | 5 | | 130 | 143 |
| | 6 | | <87 | -46 |
| | 7 | | 105 | -89 |
| | 8 | | 180 | -203 |
| 12 | 0 | 2 | 159 | -202 |
| | 1 | | 379 | -350 |
| | 2 | | 415 | 369 |
| | 3 | | 966 | 973 |
| | 4 | | 102 | 81 |
| | 5 | | <79 | 56 |
| | 6 | | 303 | 262 |
| | 7 | | 274 | 264 |
| 13 | 1 | 2 | 670 | -686 |
| | 2 | | 508 | -474 |
| | 3 | | 760 | -708 |
| | 4 | | 126 | 105 |
| | 5 | | 483 | 523 |
| 14 | 0 | 2 | 159 | -129 |
| | 1 | | 260 | 237 |
| | 2 | | 584 | 564 |
| | 3 | | 851 | -835 |
| | 4 | | 854 | -878 |
| -18 | 0 | 3 | 87 | 137 |
| | 1 | | 368 | 324 |
| | 2 | | 75 | 0 |
| -17 | 1 | 3 | 530 | -533 |
| | 2 | | 335 | 253 |
| | 3 | | 105 | 67 |
| | 4 | | 61 | 63 |
| -16 | 0 | 3 | 760 | -731 |
| | 1 | | 415 | 420 |
| | 2 | | 429 | 414 |
| | 3 | | 638 | -665 |
| | 4 | | 184 | 195 |
| | 5 | | <65 | -2 |
| | 6 | | 170 | 154 |
| -15 | 1 | 3 | 379 | -365 |
| | 2 | | 332 | -375 |
| | 3 | | 202 | -251 |
| | 4 | | 144 | 212 |
| | 5 | | 65 | -3 |
| | 6 | | 186 | -142 |
| | 7 | | 335 | -267 |
| -14 | 0 | 3 | 285 | -205 |
| | 1 | | 1060 | -1054 |
| | 2 | | 772 | 761 |
| | 3 | | 198 | -197 |
| | 4 | | 332 | 368 |
| | 5 | | 804 | -802 |
| | 6 | | 400 | -377 |
| | 7 | | 123 | -121 |
| | 8 | | 202 | 180 |
| -13 | 1 | 3 | 1673 | 1737 |
| | 2 | | 768 | 754 |
| | 3 | | 83 | 42 |
| | 4 | | 418 | 429 |
| | 5 | | 512 | 556 |
| | 6 | | 490 | 564 |
| | 7 | | 682 | -703 |
| | 8 | | <69 | -57 |
| -12 | 0 | 3 | 4568 | -4589 |
| | 1 | | 800 | 801 |
| | 2 | | 1435 | 1377 |
| | 3 | | 634 | 634 |
| | 4 | | 818 | -821 |
| | 5 | | 1150 | 1162 |
| | 6 | | 317 | 331 |
| | 7 | | 177 | 139 |
| | 8 | | 400 | 372 |
| | 9 | | <57 | -24 |
| -11 | 1 | 3 | 754 | -743 |
| | 2 | | 1421 | -1373 |
| | 3 | | 999 | -993 |
| | 4 | | 184 | -152 |
| | 5 | | 573 | 636 |
| | 6 | | 778 | -762 |
| | 7 | | 220 | -199 |
| | 8 | | 533 | 493 |
| | 9 | | 170 | -219 |
| -10 | 0 | 3 | 162 | -82 |
| | 1 | | 616 | 615 |
| | 2 | | 880 | 838 |
| | 3 | | 981 | -1026 |
| | 4 | | 134 | 99 |
| | 5 | | 605 | 617 |
| | 6 | | 736 | -677 |
| | 7 | | 231 | -231 |
| | 8 | | 180 | 166 |
| | 9 | | 206 | -170 |
| | 10 | | 714 | 662 |
| -9 | 1 | 3 | 134 | -120 |
| | 2 | | <87 | -41 |
| | 3 | | 422 | -432 |
| | 4 | | 249 | -258 |
| | 5 | | 245 | 262 |
| | 6 | | 371 | -344 |
| | 7 | | 598 | -585 |
| | 8 | | 494 | -482 |
| | 9 | | 646 | 653 |
| | 10 | | 465 | 481 |
| -8 | 0 | 3 | 674 | -636 |
| | 1 | | 346 | -346 |
| | 2 | | 1049 | 1000 |
| | 3 | | 231 | 153 |
| | 4 | | 94 | -203 |
| | 5 | | <83 | 25 |
| | 6 | | 288 | -277 |
| | 7 | | 616 | -599 |
| | 8 | | 796 | -807 |
| | 9 | | 674 | -685 |
| | 10 | | 537 | -519 |
| -7 | 1 | 3 | 260 | -270 |
| | 2 | | 162 | -180 |
| | 3 | | 1799 | 1825 |
| | 4 | | 1067 | 1063 |
| | 5 | | 883 | 822 |
| | 6 | | 371 | -348 |
| | 7 | | 750 | 750 |
| | 8 | | 778 | 734 |
| | 9 | | 375 | 319 |
| | 10 | | 891 | -879 |
| -6 | 0 | 3 | 353 | 358 |
| | 1 | | 1640 | -1597 |
| | 2 | | 584 | 544 |
| | 3 | | 584 | -556 |
| | 4 | | 736 | -716 |
| | 5 | | 923 | 905 |
| | 6 | | 858 | 867 |
| | 7 | | 404 | 410 |
| | 8 | | 1027 | -1094 |
| | 9 | | 1363 | 1332 |
| | 10 | | 1027 | 962 |
| | 11 | | 696 | 699 |
| -5 | 1 | 3 | 919 | -925 |
| | 2 | | 1914 | 1855 |
| | 3 | | 227 | -174 |
| | 4 | | 515 | -500 |
| | 5 | | 1853 | -1811 |
| | 6 | | 1463 | 1490 |
| | 7 | | 966 | -918 |
| | 8 | | 768 | -791 |
| | 9 | | 278 | 256 |
| | 10 | | 115 | -89 |
| | 11 | | 317 | 331 |
| -4 | 0 | 3 | 2794 | -2790 |
| | 1 | | 285 | -278 |
| | 2 | | 389 | 304 |
| | 3 | | 533 | -504 |
| | 4 | | 505 | -478 |
| | 5 | | 986 | 895 |
| | 6 | | 1359 | 1399 |
| | 7 | | 2448 | -2412 |
| | 8 | | 375 | 345 |
| | 9 | | 220 | 199 |
| | 10 | | 162 | 190 |
| | 11 | | 530 | -529 |
| -3 | 1 | 3 | 544 | 515 |
| | 2 | | 772 | -822 |
| | 3 | | 533 | 575 |
| | 4 | | 766 | -746 |
| | 5 | | 1197 | 1111 |
| | 6 | | 249 | -216 |
| | 7 | | 891 | -836 |
| | 8 | | 506 | 479 |
| | 9 | | 220 | 83 |
| | 10 | | 180 | -110 |
| | 11 | | 469 | -449 |
| -2 | 0 | 3 | 224 | 267 |
| | 1 | | 577 | -537 |
| | 2 | | 684 | -731 |
| | 3 | | 245 | -274 |
| | 4 | | <90 | -2 |
| | 5 | | 764 | 665 |
| | 6 | | 634 | -650 |
| | 7 | | <87 | -39 |
| | 8 | | <87 | 70 |
| | 9 | | 231 | 225 |
| | 10 | | 137 | -76 |
| | 11 | | 160 | -171 |
| -1 | 1 | 3 | 1017 | 952 |
| | 2 | | 782 | -794 |
| | 3 | | 94 | 63 |
| | 4 | | 369 | -370 |
| | 5 | | <97 | 91 |
| | 6 | | 440 | -470 |
| | 7 | | 526 | -516 |
| | 8 | | 476 | -510 |
| | 9 | | 184 | 189 |
| | 10 | | <72 | 19 |
| | 11 | | 332 | 278 |
| 0 | 0 | 3 | 660 | -673 |
| | 1 | | 948 | 1012 |
| | 2 | | 2797 | 2863 |
| | 3 | | 1403 | 1464 |
| | 4 | | 627 | -586 |
| | 5 | | 919 | 882 |
| | 6 | | 836 | 789 |
| | 7 | | 407 | 406 |
| | 8 | | 458 | -480 |
| | 9 | | 386 | -434 |
| | 10 | | <75 | -58 |
| 1 | 1 | 3 | 2289 | -2300 |
| | 2 | | 1081 | -1076 |
| | 3 | | 595 | -581 |
| | 4 | | 1918 | 1914 |
| | 5 | | 591 | 505 |
| | 6 | | 184 | -227 |
| | 7 | | 397 | 402 |
| | 8 | | 573 | 585 |
| | 9 | | 227 | 120 |
| | 10 | | 364 | 362 |
| 2 | 0 | 3 | 270 | 234 |
| | 1 | | 1276 | 1255 |
| | 2 | | 742 | -733 |
| | 3 | | 2823 | -2808 |
| | 4 | | 636 | -572 |
| | 5 | | 94 | -80 |
| | 6 | | 130 | 42 |
| | 7 | | 245 | -269 |
| | 8 | | 647 | -797 |
| | 9 | | 115 | 123 |
| | 10 | | 451 | 519 |
| 3 | 1 | 3 | 665 | 638 |
| | 2 | | 195 | -146 |
| | 3 | | 829 | 814 |
| | 4 | | 505 | 516 |
| | 5 | | 544 | -503 |
| | 6 | | <83 | 52 |
| | 7 | | 83 | 78 |
| | 8 | | 766 | -740 |
| | 9 | | 472 | 491 |
| | 10 | | 87 | 57 |
| 4 | 0 | 3 | 306 | 219 |
| | 1 | | 256 | 244 |
| | 2 | | 360 | -294 |
| | 3 | | 94 | -58 |
| | 4 | | <87 | 81 |
| | 5 | | <87 | -40 |
| | 6 | | 353 | 285 |
| | 7 | | 281 | -324 |
| | 8 | | 260 | -236 |
| | 9 | | 97 | 122 |
| 5 | 1 | 3 | <90 | -102 |
| | 2 | | 249 | -241 |
| | 3 | | 184 | 187 |
| | 4 | | 555 | 545 |
| | 5 | | <83 | 57 |
| | 6 | | 342 | -356 |
| | 7 | | 386 | -427 |
| | 8 | | 155 | 163 |
| | 9 | | 234 | -239 |
| 6 | 0 | 3 | 94 | -90 |
| | 1 | | 317 | -327 |
| | 2 | | <87 | 97 |
| | 3 | | 267 | -255 |
| | 4 | | 242 | 247 |
| | 5 | | 292 | 381 |
| | 6 | | 760 | 820 |
| | 7 | | <87 | 56 |
| | 8 | | <69 | -8 |
| 7 | 1 | 3 | 537 | 563 |
| | 2 | | <75 | 79 |
| | 3 | | <87 | -112 |
| | 4 | | 465 | -462 |
| | 5 | | 433 | -445 |
| | 6 | | 566 | 535 |
| | 7 | | <72 | -29 |
| 8 | 0 | 3 | 1283 | -1347 |
| | 1 | | 566 | 421 |
| | 2 | | 346 | 372 |
| | 3 | | 306 | 344 |
| | 4 | | 721 | -726 |
| | 5 | | 736 | 699 |
| | 6 | | 299 | -262 |
| | 7 | | 567 | -673 |
| 9 | 1 | 3 | 177 | -196 |
| | 2 | | 321 | -306 |
| | 3 | | 577 | -516 |
| | 4 | | 206 | -188 |
| | 5 | | 1009 | 1013 |
| | 6 | | 357 | -383 |
| 10 | 0 | 3 | 324 | 334 |
| | 1 | | 393 | 326 |
| | 2 | | 324 | 306 |
| | 3 | | 696 | -660 |
| | 4 | | 386 | 365 |
| 11 | 1 | 3 | <57 | 40 |
| | 2 | | 97 | -123 |
| -15 | 1 | 4 | 83 | -51 |
| | 2 | | <51 | -31 |
| -14 | 0 | 4 | 869 | -904 |
| | 1 | | 126 | -172 |
| | 2 | | 196 | -205 |
| | 3 | | 108 | 133 |
| | 4 | | 206 | -222 |
| -13 | 1 | 4 | 324 | 355 |
| | 2 | | 742 | -747 |
| | 3 | | <72 | -42 |
| | 4 | | 306 | -323 |
| | 5 | | 105 | 104 |
| -12 | 0 | 4 | 602 | 582 |
| | 1 | | 1550 | 1593 |
| | 2 | | 963 | 955 |
| | 3 | | 335 | -304 |
| | 4 | | <79 | 11 |
| | 5 | | 569 | 571 |
| | 6 | | 105 | -144 |
| -11 | 1 | 4 | 865 | -869 |
| | 2 | | 75 | -64 |
| | 3 | | 299 | 269 |
| | 4 | | 984 | 945 |
| | 5 | | 130 | -105 |
| | 6 | | 123 | -152 |
| -10 | 0 | 4 | 447 | 411 |
| | 1 | | 162 | 186 |
| | 2 | | 822 | -809 |
| | 3 | | 667 | -691 |
| | 4 | | 393 | 417 |
| | 5 | | 202 | -158 |
| | 6 | | 213 | -200 |
| | 7 | | 141 | 132 |
| -9 | 1 | 4 | 144 | 185 |
| | 2 | | <83 | -97 |
| | 3 | | 236 | 158 |
| | 4 | | 274 | 249 |
| | 5 | | 123 | -76 |
| | 6 | | <75 | 26 |
| | 7 | | <61 | -66 |
| -8 | 0 | 4 | 123 | -104 |
| | 1 | | 173 | 151 |
| | 2 | | 119 | -139 |
| | 3 | | 260 | -241 |
| | 4 | | 191 | -176 |
| | 5 | | 126 | -124 |
| | 6 | | 162 | -164 |
| | 7 | | 242 | -198 |
| -7 | 1 | 4 | 195 | -223 |
| | 2 | | 299 | 323 |
| | 3 | | 364 | 344 |
| | 4 | | 213 | 155 |
| | 5 | | 616 | -615 |
| | 6 | | 357 | -331 |
| | 7 | | <72 | 56 |
| | 8 | | 115 | -169 |
| -6 | 0 | 4 | 620 | -631 |
| | 1 | | 249 | -291 |
| | 2 | | 350 | 349 |
| | 3 | | 267 | -233 |
| | 4 | | 652 | 629 |
| | 5 | | 346 | 358 |
| | 6 | | 660 | 658 |
| | 7 | | 533 | -551 |
| | 8 | | 260 | 259 |
| -5 | 1 | 4 | 804 | 814 |
| | 2 | | 152 | -77 |
| | 3 | | 317 | -326 |
| | 4 | | 656 | -696 |
| | 5 | | 364 | 357 |
| | 6 | | 569 | 631 |
| | 7 | | 551 | -550 |
| | 8 | | 393 | 402 |
| -4 | 0 | 4 | 624 | -610 |
| | 1 | | 1020 | 989 |
| | 2 | | <87 | 3 |
| | 3 | | 90 | 11 |
| | 4 | | 270 | -301 |
| | 5 | | 1020 | 981 |
| | 6 | | 1118 | -1063 |
| | 7 | | 375 | -396 |
| | 8 | | 369 | 416 |
| -3 | 1 | 4 | 338 | -367 |
| | 2 | | 260 | -210 |
| | 3 | | 335 | -266 |
| | 4 | | 360 | 273 |
| | 5 | | 620 | 611 |
| | 6 | | 880 | -824 |
| | 7 | | 260 | 277 |
| | 8 | | <47 | -47 |
| -2 | 0 | 4 | 245 | 295 |
| | 1 | | 152 | -166 |
| | 2 | | 87 | 57 |
| | 3 | | 115 | -13 |
| | 4 | | 620 | 632 |
| | 5 | | <72 | -90 |
| | 6 | | 310 | -255 |
| | 7 | | 350 | 356 |
| -1 | 1 | 4 | 400 | -446 |
| | 2 | | 393 | -402 |
| | 3 | | 418 | -399 |
| | 4 | | 216 | 152 |
| | 5 | | 72 | -99 |
| | 6 | | <83 | -47 |
| | 7 | | <65 | -45 |
| 0 | 0 | 4 | 332 | 325 |
| | 1 | | 502 | 529 |
| | 2 | | 598 | 609 |
| | 3 | | 847 | -862 |
| | 4 | | 404 | -442 |
| | 5 | | <90 | -179 |
| | 6 | | <72 | -24 |
| | 7 | | 314 | -349 |
| 1 | 1 | 4 | 238 | 237 |
| | 2 | | 436 | 492 |
| | 3 | | 808 | 906 |
| | 4 | | 872 | 875 |
| | 5 | | 195 | -221 |
| | 6 | | 94 | -24 |
| 2 | 0 | 4 | 75 | 48 |
| | 1 | | <75 | 96 |
| | 2 | | 1193 | -1273 |
| | 3 | | 278 | -270 |
| | 4 | | 458 | 478 |
| | 5 | | 487 | 472 |
| | 6 | | 252 | 250 |
| 3 | 1 | 4 | 87 | -27 |
| | 2 | | 119 | -143 |
| | 3 | | 111 | 30 |
| | 4 | | 656 | -658 |
| | 5 | | 292 | -316 |
| 4 | 0 | 4 | 425 | 379 |
| | 1 | | 234 | -177 |
| | 2 | | <72 | 37 |
| | 3 | | 220 | 251 |
| | 4 | | <65 | 77 |
| 5 | 1 | 4 | <65 | -35 |
| | 2 | | 137 | 100 |
| | 3 | | 75 | 38 |
| 6 | 0 | 4 | 220 | -276 |

Table 3. *Coordinates as fractions of unit-cell edges*

Heavy atoms*

| | Least-squares output | | | | | | After correction for thermal motion | | |
|---|---|---|---|---|---|---|---|---|---|
| | $x$ | $y$ | $z$ | $\sigma(x)$ | $\sigma(y)$ | $\sigma(z)$ | $x'$ | $y'$ | $z'$ |
| O(1) | −0·0469 | 0·3229 | 0·3131 | 0·0001 | 0·0002 | 0·0005 | −0·0478 | 0·3240 | 0·3143 |
| O(2) | −0·0117 | 0·1575 | 0·0983 | 0·0001 | 0·0001 | 0·0005 | −0·0119 | 0·1556 | 0·0965 |
| O(3) | 0·3389 | 0·4605 | 0·2571 | 0·0001 | 0·0001 | 0·0004 | 0·3398 | 0·4611 | 0·2575 |
| N | 0·0063 | 0·2609 | 0·2067 | 0·0001 | 0·0002 | 0·0004 | 0·0059 | 0·2605 | 0·2064 |
| C(1) | 0·0933 | 0·3109 | 0·2114 | 0·0001 | 0·0001 | 0·0004 | 0·0931 | 0·3107 | 0·2112 |
| C(2) | 0·1096 | 0·4314 | 0·3008 | 0·0001 | 0·0002 | 0·0004 | 0·1094 | 0·4318 | 0·3013 |
| C(3) | 0·1926 | 0·4792 | 0·3132 | 0·0001 | 0·0001 | 0·0005 | 0·1927 | 0·4799 | 0·3138 |
| C(4) | 0·2590 | 0·4069 | 0·2393 | 0·0001 | 0·0002 | 0·0004 | 0·2594 | 0·4071 | 0·2395 |
| C(5) | 0·2417 | 0·2863 | 0·1508 | 0·0001 | 0·0002 | 0·0005 | 0·2420 | 0·2859 | 0·1503 |
| C(6) | 0·1582 | 0·2378 | 0·1331 | 0·0001 | 0·0002 | 0·0005 | 0·1582 | 0·2372 | 0·1324 |

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

Table 3 (cont.)

Hydrogen atoms*

| | Least-squares output | | | | | | Calculated† | | |
|---|---|---|---|---|---|---|---|---|---|
| | $x$ | $y$ | $z$ | $\sigma(x)$ | $\sigma(y)$ | $\sigma(z)$ | $x''$ | $y''$ | $z''$ |
| H(O) | 0·377 | 0·414 | 0·205 | 0·002 | 0·003 | 0·008 | 0·3836 | 0·4051 | 0·1959 |
| H(2) | 0·063 | 0·478 | 0·340 | 0·001 | 0·002 | 0·005 | 0·0556 | 0·4854 | 0·3461 |
| H(3) | 0·206 | 0·563 | 0·376 | 0·001 | 0·002 | 0·006 | 0·2073 | 0·5727 | 0·3825 |
| H(5) | 0·286 | 0·237 | 0·109 | 0·001 | 0·002 | 0·005 | 0·2933 | 0·2286 | 0·1017 |
| H(6) | 0·141 | 0·159 | 0·076 | 0·002 | 0·003 | 0·007 | 0·1384 | 0·1455 | 0·0671 |

* Calculated by extending C–H to 1·08 Å and O–H to 1·00 Å.

Table 4. *Final temperature factors**

| | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{23}$ | $\beta_{13}$ |
|---|---|---|---|---|---|---|
| O(1) | 0·00438 | 0·01324 | 0·1748 | 0·00026 | −0·0147 | 0·0278 |
| O(2) | 0·00640 | 0·01050 | 0·2061 | −0·00531 | −0·0243 | 0·0330 |
| O(3) | 0·00435 | 0·00843 | 0·1454 | −0·00065 | 0·0044 | 0·0205 |
| N | 0·00420 | 0·00896 | 0·1022 | −0·00070 | −0·0001 | 0·0098 |
| C(1) | 0·00376 | 0·00761 | 0·0721 | 0·00064 | 0·0010 | 0·0122 |
| C(2) | 0·00432 | 0·00737 | 0·0726 | 0·00214 | −0·0024 | 0·0124 |
| C(3) | 0·00497 | 0·00601 | 0·0846 | 0·00079 | −0·0022 | 0·0103 |
| C(4) | 0·00394 | 0·00723 | 0·0762 | 0·00064 | 0·0059 | 0·0151 |
| C(5) | 0·00435 | 0·00733 | 0·0859 | 0·00252 | 0·0015 | 0·0130 |
| C(6) | 0·00473 | 0·00612 | 0·0870 | 0·00078 | −0·0027 | 0·0129 |
| Average s.d. | 0·00006 | 0·00012 | 0·0012 | 0·00015 | 0·0007 | 0·0004 |

| | $B$ |
|---|---|
| H(O) | 6·4 |
| H(2) | 2·8 |
| H(3) | 2·7 |
| H(5) | 3·0 |
| H(6) | 5·0 |

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

As a result of the refinement with the extinction-corrected structure factors the difference map through the molecular plane improved markedly; the final map showing the hydrogen atoms is reproduced in Fig. 1(a) while Fig. 1(b) shows the electron density perpendicular to the plane of the benzene ring. Refinement was considered complete after the shifts had become random and less than one fifth of the estimated standard deviations. The agreement factors at that stage were $r = 2·15\%$ and $R = \Sigma|kF_o - |F_c||/\Sigma kF_o = 6·9\%$. Observed and calculated structure factors are listed in Table 2; final positional and temperature parameters and their standard deviations are found in Tables 3 and 4. The packing diagrams projected on (001) and (010) given in Fig. 2.

## Discussion

### Packing arrangement

Like the $\alpha$ modification the $\beta$ structure contains infinite chains of glide-plane related molecules linked to each other by hydrogen bonds. In accordance with the infrared data the OH $\cdots$ O distances in the two forms are now found to be essentially identical (2·84 Å after correction for thermal motion, as against 2·82 Å in the $\alpha$ form at 90 °K). The angle between the benzene-ring planes in adjacent molecules, which was 74°2' in the

$\alpha$ form, is now 28°0'. The planes of parallel molecules related by the $c$-axis translation being 3·43 Å apart, a large number of short contacts are found between these molecules. The intermolecular distances listed in Table 5 should be compared with the intermolecular vectors in the thermodynamically stable $\alpha$ form (Table 6 of Coppens & Schmidt, 1965). The latter was analyzed at 90 °K; comparison of its room- and low-temperature cell dimensions indicates that intermolecular distances contract by $ca.$ 2% on cooling to liquid-nitrogen temperature. Allowing for this contraction we find that the shortest intermolecular contacts are very similar in the two modifications. However, the total number of short distances is about 25% higher in the $\alpha$ form, even though the densities of the two forms differ by only 1%: in the less dense $\beta$ modification there are 19 heavy-atom contacts shorter than 3·60 Å, and 25, involving hydrogen atoms, shorter than 3·0 Å, a total of 44. In the corresponding ranges the $\alpha$ modification has, after allowance for the 2% contraction, 25 and 32 such contacts, a total of 57. This difference is also expressed in the coordination numbers of the two structures: in the $\alpha$ form every molecule makes contact with thirteen neighboring molecules, while the $\beta$ form has a coordination number of only ten if we exclude molecule V (Table 5) whose shortest contact of 3·58 Å involves two oxygen atoms. Table 5

lists only nine of these ten molecules since the contacts to the molecule at $\frac{1}{2}-x$, $\frac{1}{2}+y$, $1-z$, are symmetry related and hence identical with the contacts to molecule IX at $\frac{1}{2}-x$, $y-\frac{1}{2}$, $1-z$.

The thermodynamic relationship of the two forms thus becomes understandable: the structure with the higher coordination and the larger number of intermolecular contacts is the stable one, as predicted by Kitaigorodskii's (1957) close-packing theory.

*Molecular dimensions*

The benzene ring is planar within the experimental errors; the nitro group on the other hand, is displaced from the plane of the ring (Table 7). Similar but smaller deviations from planarity have been found in the $\alpha$ form. The main effect of non-planarity is a reduction in intermolecular distances and a corresponding in-

crease in the packing density: the distances $O(2)$--$O(1)(I)$ and $O(1)$--$N(II)$ between c-axis translation related molecules are shortened by about 0·25 and 0·15 Å to 3·40 and 3·31 Å respectively.

Intramolecular distances before and after correction for thermal motion (Cruickshank, 1961) are given in Table 6 and Fig. 3. Comparison with the distances in

Table 5. *Intermolecular distances* (Å)

Distances are given between the reference molecule of which the atomic coordinates are listed in Table 3 and surrounding molecules. Distances involving hydrogen atoms are based on calculated hydrogen coordinates given in Table 3. Values given are not corrected for thermal motion.

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

| Distances between heavy atoms $<3\cdot6$ Å | | Distances involving hydrogen atoms $<3\cdot0$ Å | |
|---|---|---|---|
| $O(2)O(1)(I)$ | 3·40 | $O(2)H(O)(III)$ | 1·89* |
| $C(6)C(1)(I)$ | 3·43 | $O(1)H(5)(III)$ | 2·42 |
| $C(4)C(3)(I)$ | 3·45 | $O(1)H(O)(III)$ | 2·74 |
| $O(1)N(II)$ | 3·31 | $NH(O)(III)$ | 2·63 |
| $O(1)C(1)(II)$ | 3·45 | $O(1)H(2)(VI)$ | 2·51 |
| $O(1)C(5)(III)$ | 3·36 | $H(2)H(2)(VI)$ | 2·36 |
| $O(3)O(2)(IV)$ | 2·86* | $H(2)H(2)(VII)$ | 2·70 |
| $O(3)O(1)(IV)$ | 3·58 | $O(3)H(6)(VIII)$ | 2·47 |
| $O(3)O(2)(V)$ | 3·58 | $C(6)H(3)(IX)$ | 2·97 |
| $O(1)C(2)(VI)$ | 3·37 | $C(5)H(3)(IX)$ | 2·93 |
| $O(1)C(3)(VII)$ | 3·52 | $H(6)H(3)(IX)$ | 2·78 |
| $O(1)C(2)(VII)$ | 3·53 | $H(5)H(3)(IX)$ | 2·61 |
| $O(3)C(6)(VIII)$ | 3·42 | $H(6)H(O)(X)$ | 2·84 |
| | | $H(5)H(3)(X)$ | 2·52 |

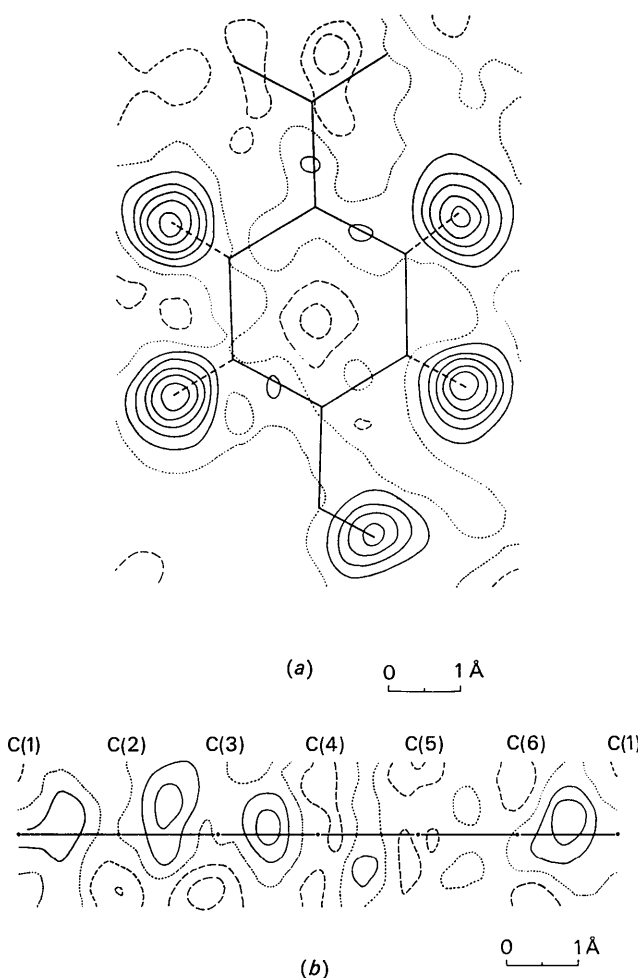* Hydrogen bond.



(a)  0    1 Å



(b)  0    1 Å

Fig. 1. (a) Difference map through molecular plane showing hydrogen atoms. The molecular frame is based on the least-squares coordinates. Contours every 0·1 e.Å$^{-3}$, zero contour dotted, negative contours broken. (b) Difference map through unfolded benzene ring, perpendicular to molecular plane. Contours each 0·05 e.Å$^{-3}$, zero contour dotted, negative contours broken. Local maxima are discernible in the middle of the bonds.
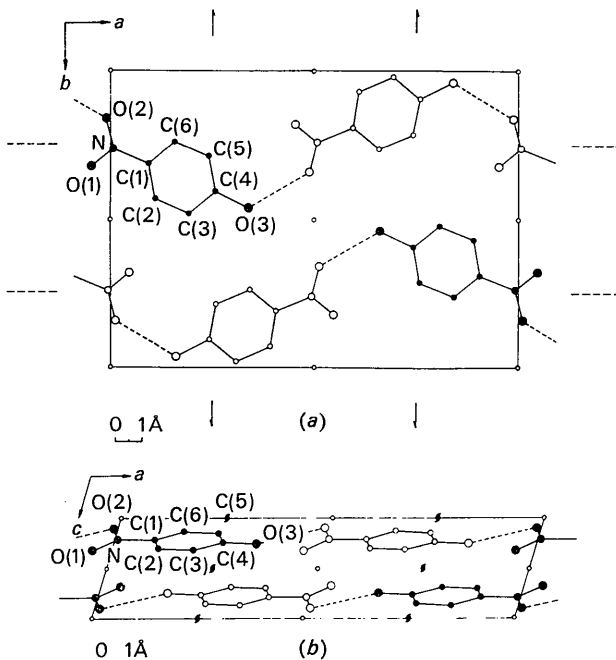


0  1A  (a)



0  1A  (b)

Fig. 2. Packing diagrams. (a) projection on (001), (b) projection on (010).

Table 6. *Intramolecular distances and their standard deviations*

| Bond | Before correction for thermal motion | s.d. | After correction for thermal motion | s.d.* | Corresponding distance in $\alpha$-$p$-nitrophenol at 90°$K$ (not corrected for thermal motion) |
|------|------|------|------|------|------|
| N O(1) | 1·226 | 0·002₅ | 1·243 | 0·005 | 1·232 |
| N O(2) | 1·225 | 0·002₅ | 1·241 | 0·005 | 1·236 |
| N C(1) | 1·446 | 0·002₄ | 1·450 | 0·003 | 1·442 |
| C(1)C(2) | 1·386 | 0·002₃ | 1·394 | 0·003 | 1·388 |
| C(2)C(3) | 1·373 | 0·002₃ | 1·378 | 0·003 | 1·377 |
| C(3)C(4) | 1·392 | 0·002₃ | 1·399 | 0·003 | 1·387 |
| C(4)C(5) | 1·388 | 0·002₃ | 1·396 | 0·003 | 1·393 |
| C(5)C(6) | 1·377 | 0·002₄ | 1·382 | 0·003 | 1·380 |
| C(6)C(1) | 1·386 | 0·002₃ | 1·393 | 0·003 | 1·383 |
| O(3)C(4) | 1·352 | 0·002₂ | 1·361 | 0·003 | 1·351 |

* Standard deviation in corrected bond length calculated assuming a 25 % inaccuracy in the correction.

$\alpha$-$p$-nitrophenol, listed in the last column of Table 6, shows that the bond lengths in the two molecules are equal within the experimental errors. For the $\beta$ modification the standard deviations are smaller and thus additional features become apparent: the shortening of the two C–C bonds parallel to the long molecular axis, present but not significant in the $\alpha$ form, is highly significant in the $\beta$ structure. This shortening, also observed in $p$-nitroaniline (Trueblood, Goldish & Donohue, 1961), can be attributed to contributions of quinonoid resonance structures. Resonance contributions are also likely to be responsible for the shortening of the two exocyclic bonds C–N and C–O from the single bond values of 1·475 Å and 1·43 Å (Sutton, 1958) to the observed lengths 1·450 Å and 1·361 Å. The relatively smaller contraction of the C–N bond is probably due here as in $p$-nitroaniline to non-bonded interactions between the oxygen atoms and the carbon atom carrying the nitro group (Trueblood, Goldish & Donohue, 1961). This interpretation is independently confirmed by the correlation between the C–N bond

lengths and the O–N–O angles in several aromatic nitro compounds (Coppens, 1962).

In both $p$-nitrophenol structures the nitro group is strictly symmetrical, even though one of its two oxygen atoms is hydrogen bonded. According to Table 8 the N–O bond length remains uninfluenced by hydrogen bonding as long as the O $\cdots$ HX distance (X=O: $p$-nitrophenol, X=N: $p$-nitroaniline) is 2·8 Å or larger; at shorter distances, as in the intramolecular O $\cdots$ O bond (2·497 Å) of dilituric acid (Bolton, 1963) the nitro group becomes asymmetric: the N–O bond pointing towards the proton donor is lengthened while the other bond remains essentially unaffected.

A striking feature of the molecular structure is the inequality of the two C–C–O angles. The same effect has been observed in other compounds such as resorcinol (Robertson, 1936; Bacon & Curry, 1956) and phloroglucinol (Moe, 1963); it has been interpreted by Hirshfeld (1964) as evidence for bent orbitals resulting from the repulsion between the hydrogen atom and the carbon carrying the hydroxyl group (Fig. 4).

## Thermal motion

The large temperature factors of the oxygen atoms indicate that the molecule as a whole is not a rigid body. It seems likely, however, that the remainder of the molecule is almost rigid, and on this assumption the temperature factors have been analyzed. By assuming $C_6N$ rather than the benzene ring only to be a rigid body one avoids the difficulties resulting from the approximate hexagonal symmetry of the benzene ring (Cox, Cruickshank & Smith, 1958). The rigid-body analysis was carried out by a least-squares procedure

Table 7. *Equations of planes*

Benzene ring: $0\cdot9659x - 2\cdot6902y + 3\cdot4340z + 0\cdot0236 = 0$
Nitro group: $2\cdot0830x - 3\cdot7421y + 3\cdot2219z + 0\cdot2971 = 0$
Angle between the two planes: 7°9′
The benzene ring plane is derived according to Schomaker, Waser, Marsh & Bergman (1959).

Out of plane displacements

| Atom | from benzene ring |
|------|------|
| O(1) | 0·185 |
| O(2) | −0·074 |
| N | 0·038 |
| O(3) | −0·005 |
| C(1) | 0·003 |
| C(2) | 0·002 |
| C(3) | −0·004 |
| C(4) | 0·001 |
| C(5) | 0·005 |
| C(6) | −0·006 |
| H(2) | −0·03 |
| H(3) | −0·00 |
| H(5) | 0·04 |
| H(6) | −0·00 |
| H(O) | −0·02 |

| | from NO₂ |
|------|------|
| C(1) | 0·009 |

Table 8. N–O *bond lengths in some aromatic nitro compounds* (Å)

| | | | Reference |
|------|------|------|------|
| Dilituric acid | 1·239* | 1·276* | Bolton, 1963 |
| $\beta$-$p$-Nitrophenol | 1·243 | 1·241 | |
| $p$-Nitroaniline | 1·246 | 1·247 | Trueblood, Goldish & Donohue, 1961 |
| $o$-Nitrobenzaldehyde | 1·241 | 1·249 | Coppens, 1964 |

* Bond lengths in the original article were not corrected for thermal motion. We have assumed the correction to be the same as in $p$-nitrophenol and $p$-nitroaniline (0·017 Å).
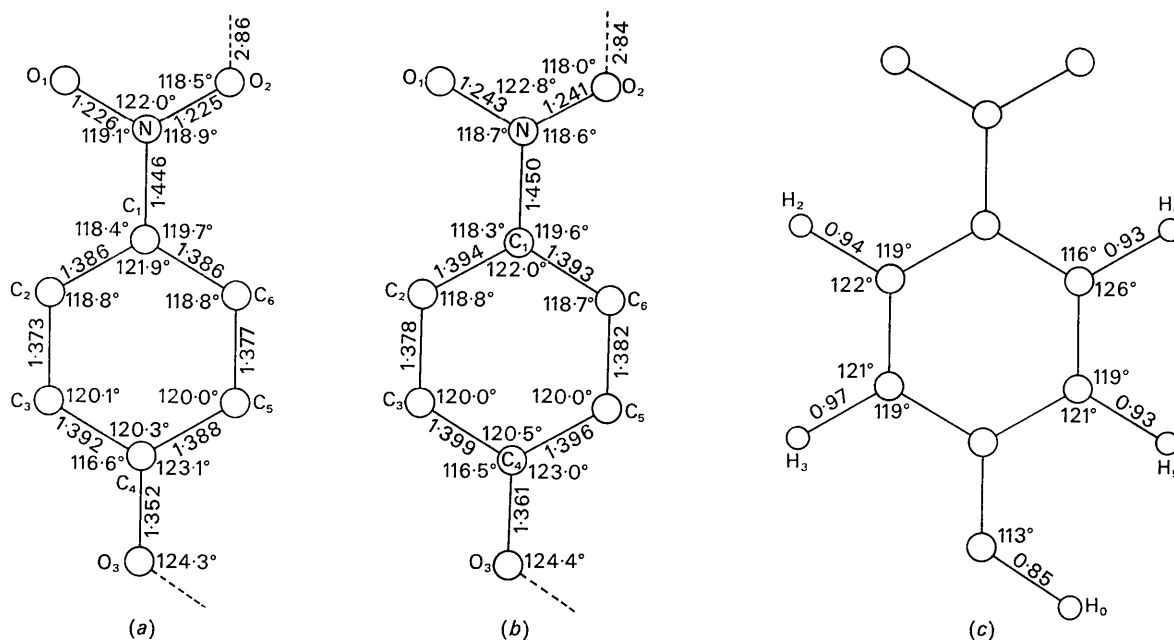
Fig. 3. Intramolecular bond lengths and angles. (a) before correction for thermal motion, (b) after correction, (c) dimensions involving hydrogens (uncorrected).

in which 42 thermal parameters were used to determine six elements each of the tensors **T** and **ω**, describing respectively the translational vibrations and the librations of the rigid body, and the three coordinates of the center of librations (Hirshfeld, Sandler & Schmidt, 1963). Results are given in Table 9; the observed and calculated elements $V_{ij}$ of the atomic vibration tensors in the molecular coordinate system are found in Table 10. The fit is satisfactory, but the estimate of $\sigma$ $(V_{ij})$ obtained from

$$\sqrt{\left(\frac{\Sigma \, [V_{ij}(\text{obs}) - V_{ij}(\text{calc})]^2}{n-s}\right)}$$

($n$ = number of observations, $s$ = number of parameters)
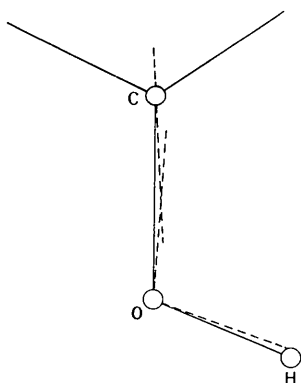


Fig. 4. The explanation of the inequality of the two C–C–O angles as given by Hirshfeld (1964). Broken lines represent the axes of the orbitals: full lines are interatomic vectors. Repulsion of the hydrogen and carbon atoms results in bending of the orbitals in the C–O bond, as the angle between the orbitals opens up less the than angle between the interatomic vectors. The orbital at the carbon atom bisects the C–C bonds.

equals 0·0026 Å², about twice the standard deviations of the $V_{ij}$(obs) as estimated from the structure-factor refinement. This may indicate that the group C₆N is not quite rigid. Alternatively, the temperature factors may be affected by bonding anisotropy, evidence for which is provided by the local maxima at the mid-points of the bond in the difference map (Fig. 1(b)). The translational vibrations of the molecule are almost isotropic; the direction of maximum vibration makes an angle of 16° with the long $a$ axis. The main libration has an r.m.s. amplitude of 5·5° and is around the long axis of the molecule, the off-diagonal elements of the ω tensor not differing significantly from zero. The extra motion of the oxygen atoms can be interpreted as a torsional oscillation of the nitro group with an r.m.s. amplitude of 11·2° and a wagging motion of the hydroxylic oxygen out of the plane of the benzene ring with an r.m.s. amplitude of 5·8°. These amplitudes are calculated on the assumption that the rigid-body motion and the internal vibration are phase independent. The torsional oscillation of the nitro group seems to be characteristic of aromatic nitro compounds (Trueblood, Goldish & Donohue, 1961).

### Structure dependence of the redox reaction

If the initial step of the photochemical reaction of α-p-nitrophenol is of the redox type (equation 1) then the difference in reactivity between the two modifications must be sought in the type of CH · · · ON contact between molecules. We note that the contact *distances* are roughly equal in the two structures and are nowhere abnormally short. However, the two modifications differ significantly in the *angles* between the C · · · O vectors and the planes of the benzene rings.

Table 9. *Rigid body motion of group* $C_6N$

Axis of inertia
Component along

| Axis | a | b | c | Direction |
|---|---|---|---|---|
| | (as fractions of unit cell edges) | | | |
| 1 | 0·06047 | 0·03463 | 0·00799 | nearly coincides with line C(4)–N |
| 2 | −0·01973 | 0·08018 | 0·06836 | perpendicular to 1 in mean plane through $C_6N$ |
| 3 | 0·02380 | −0·02151 | 0·26765 | perpendicular to mean plane |

Coordinates of center of gravity: $x = 0·1515$ $y = 0·3448$ $z = 0·2222$

T and ω tensors referred to axes of inertia

$$10^4 T \ (\text{Å}^2) = \begin{pmatrix} 462 & 26 & -7 \\ & 365 & 24 \\ & & 400 \end{pmatrix} \pm \begin{pmatrix} 11 & 7 & 9 \\ & 12 & 9 \\ & & 27 \end{pmatrix}$$

$$10^4 \omega \ (\text{rad}^2) = \begin{pmatrix} 91 & -10 & -6 \\ & 38 & -4 \\ & & 38 \end{pmatrix} \pm \begin{pmatrix} 19 & 8 & 7 \\ & 7 & 3 \\ & & 4 \end{pmatrix}$$

$$\text{Coordinates of center of librations (Å)} = \begin{pmatrix} 0·19 \\ 0·08 \\ 0·01 \end{pmatrix} \pm \begin{pmatrix} 0·08 \\ 0·06 \\ 0·08 \end{pmatrix}$$

Table 10. *Observed and calculated values of tensor elements describing thermal motion of individual atoms* (Å)

Tensors refer to axes of inertia of the rigid body $C_6N$ defined in Table 9.

| | | $10^4 V_{11}$ | $10^4 V_{22}$ | $10^4 V_{33}$ | $10^4 V_{12}$ | $10^4 V_{23}$ | $10^4 V_{13}$ |
|---|---|---|---|---|---|---|---|
| N | obs. | 450 | 578 | 668 | 11 | 34 | −21 |
| | calc. | 463 | 618 | 663 | 18 | 46 | −6 |
| C(1) | obs. | 439 | 456 | 471 | 39 | 17 | −13 |
| | calc. | 463 | 415 | 454 | 22 | 28 | −8 |
| C(2) | obs. | 532 | 382 | 513 | 69 | 0 | −11 |
| | calc. | 510 | 373 | 513 | 47 | 29 | 3 |
| C(3) | obs. | 547 | 374 | 560 | −32 | 27 | 2 |
| | calc. | 510 | 394 | 567 | −12 | 21 | −2 |
| C(4) | obs. | 442 | 475 | 473 | 20 | 66 | 12 |
| | calc. | 462 | 459 | 495 | 30 | 33 | −6 |
| C(5) | obs. | 525 | 392 | 558 | 86 | 42 | 22 |
| | calc. | 524 | 396 | 556 | 70 | 34 | 8 |
| C(6) | obs. | 521 | 371 | 578 | −16 | 25 | 1 |
| | calc. | 526 | 373 | 573 | 3 | 18 | 1 |
| O(1) | obs. | 499 | 675 | 1209 | 183 | −34 | −52 |
| | calc. | 501 | 742 | 812 | 145 | 71 | 28 |
| O(2) | obs. | 506 | 680 | 1449 | −103 | −68 | −2 |
| | calc. | 513 | 754 | 983 | −114 | 22 | −25 |
| O(3) | obs. | 421 | 591 | 916 | 11 | 139 | 26 |
| | calc. | 462 | 689 | 731 | 24 | 54 | −7 |
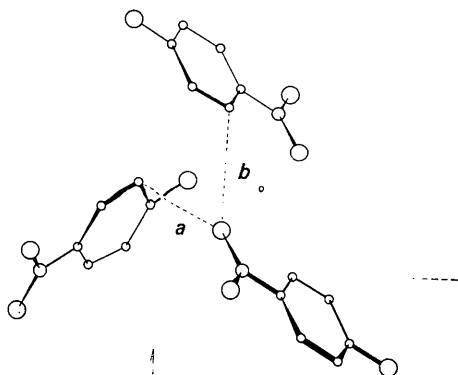


Fig. 5. A perspective view of the packing of three molecules in α-p-nitrophenol, to illustrate two types of C–H ⋯ O–N contacts. *a*: nearly linear contact common to the α and β forms; *b*: near-perpendicular contact characteristic of the α form only and regarded as responsible for the redox reaction.
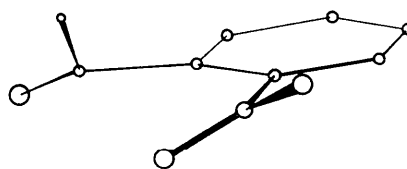


Fig. 6. A perspective view of the o-nitrobenzaldehyde molecule showing the "reactive" configuration of the N–O ⋯ C–H group. (Only the hydrogen atom attached to the aldehyde group is shown.)

In the lightstable (β) form this angle is maximally 18·5°, whereas in the light sensitive (α) modification this angle is maximally 72·8°. In the former, a hydrogen atom is therefore always interposed between a carbon atom and its nearest oxygen of a nitro group (Fig. 5), and may thereby prevent the attack by a photochemically excited oxygen atom. This interpretation suggests that the steric course of the redox reaction resembles

that of a bimolecular substitution reaction in which the attacking group approaches the reactive center from the side not occupied by another substituent. This interpretation is further supported by the structure analysis of o-nitrobenzaldehyde (Fig. 6) (Coppens & Schmidt, 1964; Coppens, 1964) in which the non-planarity of the molecule provides a similar arrangement of the reactive centers C–H and N–O.

We wish to thank Dr. F. L. Hirshfeld, who assisted with the collection of the intensities and gave valuable advice at various stages of the calculations.

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# The Structure of α-Chlorohemin*

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Chlorohemin, $C_{34}H_{32}N_4O_4FeCl$, forms soft, lath-shaped crystals of the α modification, space group $P1$ or $P\bar{1}$, $Z=2$, $a=11\cdot49$, $b=14\cdot10$, $c=10\cdot85$ Å, $\alpha=98\cdot56°$, $\beta=108\cdot49°$, $\gamma=107\cdot65°$. Three-dimensional Mo $K\alpha$ data were collected with a spectrogoniometer. The iron and chlorine atoms, located through Patterson syntheses and superposition functions, were used to initiate determination of the structure largely through $F_o-F_c$ syntheses. Full-matrix least-squares refinement and concurrent $F_o-F_c$ refinement reduced the value of $R$ to 0.095 for the 1566 observed reflections.

The iron atom of chlorohemin lies out of the plane of the four nitrogen atoms toward the chlorine atom. While each of the pyrrole residues is planar, the porphyrin ring is slightly puckered. The two vinyl residues per molecule were not located unambiguously; they are disordered in pairs, or non-centrosymmetrically arranged, in the unit cell.

## Introduction

Metallo-porphyrins are among the most ancient, universal, and extensively studied prosthetic groups of proteins (Lemberg & Legge, 1949). Nonetheless, at-

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tempts to determine mechanisms of actions of hemo-proteins have been frustrated by lack of knowledge of configurational details of the porphyrins and bonding states of the iron atom (Falk, Lemberg & Morton, 1961). It was accordingly decided to undertake the determination of several iron porphyrin structures in this laboratory. Chlorohemin was chosen as the first of these because of the extensive chemical studies upon it and because of its biological importance as an iron protoporphyrin IX compound.