bone-like pattern. Along **a**, the molecular arrangement consists of alternate, antiparallel molecules of *A* and *B* extending infinitely.

In the structure there are 161 intermolecular contact distances less than 4 Å, but none of them is abnormally short. Molecule *A* is surrounded by 14 neighbouring molecules with contact distances less than 4 Å. Molecule *B*, however, has only 10 neighbours and this difference in the number of nearest neighbours could be related to the disorder observed in molecule *B*.

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# Structural Studies of Benzene Derivatives.
# II.* Refinement of the Crystal Structure of *p*-Nitrobenzoic Acid

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The crystal structure of *p*-nitrobenzoic acid, determined by Indian workers from photographic data [Sakore & Pant, *Acta Cryst.* (1966), **21**, 715–719; Tavale & Pant, *Acta Cryst.* (1971), B**27**, 1479–1481], has been refined by full-matrix least squares to a final *R* of 0·040, with 1473 independent non-zero reflexions measured on an automated single-cystal diffractometer. Crystals are monoclinic, space group $A2/a$, with $a$ = 12·918 (2), $b$ = 5·042 (2), $c$ = 21·298 (6) Å, $\beta$ = 96·66 (2)°, $Z$ = 8. The six-membered C ring has $C_{2v}$ (*mm*) symmetry, within experimental error; the deviations from $D_{6h}$ (6/*mmm*) symmetry are interpreted as the substituent effect of the nitro-group. The internal angles at the *ipso* atoms are: $\alpha_{NO_2}$ = 123·3 (1), $\alpha_{COOH}$ = 120·4 (1)°.

## Introduction

As a development of a research programme on the deformations, induced by substitution, of the geometry of the benzene ring (Domenicano, Vaciago & Coulson, 1975*a*,*b*; Domenicano, Mazzeo & Vaciago, 1976) we have started accurate experimental work to determine the molecular structures of a number of benzene derivatives (Colapietro, Di Rienzo, Domenicano, Foresti Serantoni & Riva di Sanseverino, 1976; Domenicano, Foresti Serantoni & Riva di Sanseverino, 1977). In the present paper we describe the molecular structure of crystalline *p*-nitrobenzoic acid, as obtained from a new X-ray diffraction study.

The crystal structure of *p*-nitrobenzoic acid was originally determined by Indian workers (Sakore & Pant, 1965, 1966; Tavale & Pant, 1971). The final refinement, based on 744 reflexions from photographic records, was by block-diagonal least squares and led to average standard deviations in the bond lengths and angles of the C skeleton of 0·006 Å and 0·4° respectively. We deemed the precision of the analysis to be below the standard required for a study of the struc-

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[*] Part I: Domenicano, Foresti Serantoni & Riva di Sanseverino (1977).

tural effects of substitution, and have carried out a full-matrix least-squares refinement with a new set of diffractometer data.

## Experimental

Pale yellow, prismatic crystals were grown by evaporation of an ethanolic solution of the commercial product (Fluka). A crystal, *ca* 0·57 × 0·36 × 0·19 mm, was mounted on a Syntex $P2_1$ single-crystal diffractometer. Accurate values for the cell parameters were derived by a least-squares fit to the measured $\theta$ values for 15 accurately centred reflexions. The values obtained are compared in Table 1 with those given by previous workers.

Intensities were collected at room temperature with the $\omega$-scan technique, using Si-monochromatized Mo $K\alpha$ radiation. The scanning interval was 1·2°; the scanning speed was varied according to the intensity from a minimum value of 0·03° s$^{-1}$. 2230 independent reflexions in the $\theta$ range 2–30° were measured; 1473 of them had $I \geq 3\sigma(I)$ and were considered as observed and used in the refinement.* Three standard reflexions were monitored every 80 reflexions; their intensities indicated no counter or crystal instability. The intensities were corrected for Lorentz and polarization effects, but not for the extinction or absorption ($\mu$ for Mo $K\alpha$ is only 1·46 cm$^{-1}$; the distortion effect of absorption on the molecular parameters should, therefore, be negligible, notwithstanding the size and anisotropy of the crystal used).

## Refinement

A structure factor calculation based on the positional parameters for the non-H atoms given by Tavale & Pant (1971), and with $\bar{B} = 2·65$ Å$^2$ from a Wilson plot, gave an $R$ of 0·152. This was reduced to 0·107 by block-diagonal isotropic least-squares refinement, and then to 0·071 by anisotropic refinement. At this stage, a difference synthesis computed from terms with sin $\theta/\lambda \leq 0·40$ showed all the H atoms as well-defined peaks, in positions reasonably close to those given by Tavale & Pant (1971). Their introduction in a structure factor calculation lowered $R$ to 0·053.

The final refinement of all the atomic parameters, including the positional and isotropic thermal parameters of the H atoms, was carried out by full-matrix least squares and led to an $R$ of 0·040 ($R_w$ = 0·044). The function minimized was $\Sigma\, w(|F_o| - K|F_c|)^2$; the weighting scheme, based on the experimental $\sigma(F_o)$ derived from counting statistics, gave a reasonably low dispersion for the mean values of the minimized function over ranges of either $F_o$ or sin $\theta/\lambda$. In the last cycle all the shifts were less than 0·04$\sigma$ (non-H atoms) or 0·15$\sigma$ (H atoms). The number of observations per refined parameter was 1473/129 = 11·4.

The scattering factors of Cromer & Mann (1968) were used for O, N, and C. For H the values used were those of Hanson, Herman, Lea & Skillman (1964).

Table 1. *Crystal data*

*p*-Nitrobenzoic acid, $C_7H_5NO_4$, FW 167·12. Monoclinic, space group $A2/a$, $Z$ = 8. M.p. = 237–239°C

| | This work† | Thakar, Kapadia & Prasad (1940) | Sakore & Pant (1965) |
|---|---|---|---|
| $a$ (Å) | 12·918 (2) | 12·95 | 12·97 |
| $b$ (Å) | 5·042 (2) | 5·04 | 5·07 |
| $c$ (Å) | 21·298 (6) | 21·31 | 21·43 |
| $\beta$ (°) | 96·66 (2) | 96·6 | 96·4 |
| $V$ (Å$^3$) | 1377·8 (6) | 1382 | 1400 |
| $D_c$ (g cm$^{-3}$) | 1·611 | 1·606 | 1·585 |
| $D_m$ (g cm$^{-3}$) | — | 1·61 | 1·60 |

† Standard deviations are given in parentheses as units in the last digit. The radiation used was Mo $K\alpha$ ($\lambda$ = 0·71069 Å).

Table 2. *Final coordinates* (×10$^5$) *for non-hydrogen atoms*

Estimated standard deviations from the final full-matrix least-squares cycle are given in parentheses as units in the last digit.

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| O(1) | 54626 (7) | 24071 (23) | 4859 (5) |
| O(2) | 37953 (8) | 15699 (21) | 1501 (5) |
| O(3) | 38241 (9) | 118003 (24) | 25056 (6) |
| O(4) | 22878 (8) | 117248 (22) | 19844 (5) |
| N | 31866 (9) | 109555 (23) | 20832 (5) |
| C(1) | 41634 (10) | 49889 (26) | 9001 (6) |
| C(2) | 49016 (10) | 64166 (29) | 12929 (7) |
| C(3) | 45878 (11) | 83736 (28) | 16874 (6) |
| C(4) | 35335 (10) | 88611 (26) | 16708 (6) |
| C(5) | 27832 (10) | 75006 (31) | 12842 (6) |
| C(6) | 31063 (10) | 55243 (29) | 8957 (6) |
| C(7) | 45264 (9) | 28731 (27) | 4923 (6) |

Table 3. *Final coordinates* (×10$^4$) *and isotropic thermal parameters for hydrogen atoms*

Estimated standard deviations from the final full-matrix least-squares cycle are given in parentheses as units in the last digit.

| | $x$ | $y$ | $z$ | $B$ (Å$^2$) |
|---|---|---|---|---|
| H(O) | 4104 (15) | 62 (47) | −105 (9) | 4·4 (5) |
| H(2) | 5630 (12) | 6066 (33) | 1292 (7) | 1·3 (3) |
| H(3) | 5093 (12) | 9426 (32) | 1959 (6) | 1·3 (3) |
| H(5) | 2075 (11) | 7903 (35) | 1303 (7) | 1·3 (3) |
| H(6) | 2592 (12) | 4507 (32) | 627 (7) | 1·4 (3) |

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* The reflexions 202, 015, 11$\bar{5}$ and 21$\bar{3}$ were too intense to be measured accurately and were excluded from the data set.

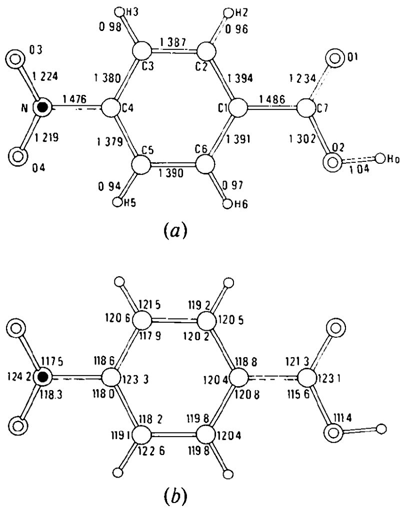

Fig. 1. Molecular geometry of *p*-nitrobenzoic acid: (*a*) bond lengths (Å), (*b*) bond angles (°). Estimated standard deviations (calculated from the standard deviations in the atomic parameters given in Tables 2 and 3) are 0·002 Å for C–C, C–N, C–O and N–O bonds, 0·02 Å for C–H and O–H bonds, 0·1° for angles not involving H atoms, 1·0° for angles involving H atoms.

The data reduction was performed on an HP 21MX minicomputer. All other calculations were carried out on the Univac 1110 computer of the University of Rome with local crystallographic programs (Carruthers & Spagna, 1975).

## Results and discussion

The final atomic parameters are given in Tables 2 and 3.* Bond lengths and angles are given in Fig. 1. The equation of the least-squares plane through the six C atoms of the ring and the displacements of all the atoms from this plane are given in Table 4. Torsion angles are reported in Table 5.

### *The six-membered* C *ring*

The symmetry of the C ring is $C_{2v}$ (*mm*), within experimental error. The most significant deviations from $D_{6h}$ (6/*mmm*) symmetry concern the half of the ring nearest to the $-NO_2$ substituent, and comprise: (i) a shortening (by *ca* 0·01 Å, 5σ) of the C(3)–C(4) and C(4)–C(5) bonds, with respect to the other four C–C bonds; (ii) an increase from 120° (by 3·3°, 33σ) of the C(3)–C(4)–C(5) bond angle; and (iii) a decrease from 120° (by *ca* 2°, 20σ) of the C(2)–C(3)–C(4) and C(4)–C(5)–C(6) bond angles. All the effects are consistent with the strong σ-electron-withdrawing character of the $-NO_2$ group (Domenicano, Vaciago & Coulson, 1975*a*).

Table 4. *Deviations from planarity*

Equation of the least-squares plane through the six C atoms of the ring (referred to the crystallographic axes): $1{\cdot}8081x + 3{\cdot}4086y - 15{\cdot}6497z = 1{\cdot}0459$. The standard deviations in the atomic positions are 0·0010–0·0014 Å for the non-H atoms, 0·015–0·021 Å for the H atoms.

Displacements (Å) of atoms from the plane

| | | | | | |
|---|---|---|---|---|---|
| C(1)* | −0·001 | C(7) | −0·019 | H(2) | 0·02 |
| C(2)* | 0·004 | N | 0·004 | H(3) | 0·02 |
| C(3)* | −0·003 | O(1) | 0·002 | H(5) | −0·02 |
| C(4)* | −0·001 | O(2) | −0·059 | H(6) | −0·02 |
| C(5)* | 0·004 | O(3) | −0·253 | H(O) | −0·12 |
| C(6)* | −0·003 | O(4) | 0·259 | | |

* Atoms defining the least-squares plane.

The lengths of the four C–C bonds other than C(3)–C(4) and C(4)–C(5) range from 1·387 to 1·394 Å. Their mean value, 1·391 (1) Å, is somewhat lower than the value generally accepted for benzene itself, 1·398 Å;* this, however, may be an effect of thermal motions in the crystal. The peculiar shortening of the central C C bonds reported by Tavale & Pant (1971) is not confirmed by the present, more accurate study.

The internal angles at the *ipso* atoms, $\alpha_{NO_2}$ = 123·3 (1)° and $\alpha_{COOH}$ = 120·4 (1)°, are both slightly greater than the corresponding mean values reported by Domenicano, Mazzeo & Vaciago (1976), namely 122·1 and 119·8°.

### *The substituents*

The geometries of the $-NO_2$ and $-COOH$ groups, including the lengths of the C–substituent bonds, are

Table 5. *Torsion angles* (°)

Signs have been given according to the convention of Klyne & Prelog (1960). Estimated standard deviations are *ca* 0·1°.

(*a*) $-NO_2$ substituent

| | | | |
|---|---|---|---|
| O(3)–N–C(4)–C(3) | −13·9 | O(4)–N–C(4)–C(5) | −13·2 |
| O(3)–N–C(4)–C(5) | 166·5 | O(4)–N–C(4)–C(3) | 166·4 |

(*b*) $-COOH$ substituent

| | | | |
|---|---|---|---|
| O(1)–C(7)–C(1)–C(2) | −1·6 | O(2)–C(7)–C(1)–C(6) | −1·2 |
| O(1)–C(7)–C(1)–C(6) | 179·0 | O(2)–C(7)–C(1)–C(2) | 178·2 |

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32446 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

* Values in the narrow range 1·397–1·399 Å have been obtained by many authors using different techniques for the C–C bond length of unsubstituted benzene. The techniques used comprise Raman spectroscopy (Stoicheff, 1954; Langseth & Stoicheff, 1956), gas-phase electron diffraction (Almenningen, Bastiansen & Fernholt, 1958; Kimura & Kubo, 1960; Bastiansen, Fernholt, Seip, Kambara & Kuchitsu, 1973; Tamagawa, Iijima & Kimura, 1976) and low-temperature neutron diffraction (Bacon, Curry & Wilson, 1964).

consistent with those observed in many other substituted derivatives of nitrobenzene and benzoic acid, respectively, and will not be discussed in detail.

Each of the two substituents is strictly coplanar with the C atom of the ring to which it is bonded. Coplanarity with the C hexagon is, however, far from being attained in the case of $-NO_2$, and only approximate in the case of $-COOH$. The dihedral angles between the planes of the substituents and the least-squares plane of the ring are indeed 13·7° for $-NO_2$ and 1·8° for $-COOH$. In the case of $-NO_2$ the lack of coplanarity with the ring is essentially due to a twist about the C(4)—N bond (Table 5).

The H atom of the $-COOH$ group has been unequivocally located near O(2) and successfully refined, with no evidence whatsoever of occupational disorder. This is in keeping with the marked differences in the lengths of the two C—O bonds and in the values of the C—C—O angles (Fig. 1). The lack of axial symmetry in the $-COOH$ group is presumably responsible for the small in-plane bending of the C(1)—C(7) bond [the C(7)—C(1)—C(2) angle is 2·0° smaller than C(7)—C(1)—C(6)]. Note that C(7) is also 0·019 Å out of the ring plane. No such bendings are observed with the $-NO_2$ group, which has almost perfect $C_{2v}$ (*mm*) symmetry.

### *The hydrogen bonding*

The molecules of *p*-nitrobenzoic acid are hydrogen-bonded in pairs across a centre of symmetry (Sakore & Pant, 1965, 1966). The geometrical parameters obtained here for the O(2)—H(O)···O(1′) hydrogen bond are: distances O(2)···O(1′) = 2·660 (2); O(2)—H(O) = 1·04 (2); H(O)···O(1′) = 1·62 (2) Å; angle O(2)—H(O)···O(1′) = 177 (2)°.*

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* The symmetry operation relating O(1′) to O(1) is $1-x, -y, -z$.

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