

- LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* **A30**, 580–584.
- REY-LAFON, M. (1979). *J. Chem. Phys.* **71**, 5324–5328.
- REY-LAFON, M. & LAGNIER, R. (1975a). *C. R. Acad. Sci. Sér. C*, **280**, 547–550.
- REY-LAFON, M. & LAGNIER, R. (1975b). *Mol. Cryst. Liq. Cryst.* **32**, 13–16.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- STOLEVIK, R. & RADEMACHER, P. (1969). *Acta Chem. Scand.* **23**, 672–682.
- TERAUCHI, H., SAKAI, T. & CHIHARA, H. (1975). *J. Chem. Phys.* **62**, 3832–3833.
- TRINQUECOSTE, C., REY-LAFON, M. & FOREL, M. T. (1974). *Spectrochim. Acta Part A*, **30**, 813–826.
- TROUGHTON, P. G. H. (1969). *Practical Experience in Working with a Siemens Automatic Single-Crystal Diffractometer*, Department of Chemical Crystallography, Imperial College, London SW7, England.
- WRIGHT, A. & BERNERON, M. (1980). *Nucl. Instrum. Methods*. To be published.

Acta Cryst. (1980). **B36**, 586–591

Structural Studies of Benzene Derivatives.

VIII.* Refinement of the Crystal Structure of *p*-Dinitrobenzene

BY FERNANDA DI RIENZO AND ALDO DOMENICANO

Istituto di Chimica Farmaceutica e Tossicologica, Università di Roma, Città Universitaria, 00185 Roma and Laboratorio di Strutturistica Chimica del CNR 'Giordano Giacomello', 00016 Monterotondo Stazione, Italy

AND LODOVICO RIVA DI SANSEVERINO

Istituto di Mineralogia e Petrografia, Università di Bologna, Piazza San Donato 1, 40127 Bologna, Italy

(Received 7 August 1979; accepted 18 September 1979)

Abstract

$C_6H_4N_2O_4$ is monoclinic, space group $P2_1/n$, with $a = 11.137$ (2), $b = 5.461$ (1), $c = 5.684$ (3) Å, $\beta = 92.22$ (4)°, $Z = 2$. The final R is 0.0408 for 559 independent counter intensities. The benzene ring has *mmm* symmetry within experimental error. The distortions from *6/mmm* symmetry are quite marked, and involve bond lengths as well as angles; they testify to the strong σ -electron-withdrawing character of the substituent. The value of the internal angle at the *ipso* atom, $\alpha_{NO_2} = 123.4$ (1)°, is in good agreement with values reported for other molecules where the nitro group is *para* to a π acceptor.

Introduction

The structures of several *para*-substituted derivatives of nitrobenzene, *p*- $X-C_6H_4-NO_2$, are being studied in our laboratories to investigate the effect of X on the ring distortions caused by the nitro group. Results have been presented for *p*-nitrobenzoic acid (Colapietro & Domenicano, 1977) and *p*-nitrobenzamide (Di Rienzo, Domenicano & Foresti Serantoni, 1977); here we

report the structure of *p*-dinitrobenzene. A preliminary communication has been given (Colapietro, Di Rienzo, Domenicano, Portalone & Riva di Sanseverino, 1977).

The beautiful, well formed crystals of *p*-dinitrobenzene have stimulated the interest of X-ray crystallographers for half a century. Pioneering work was done by Hertel & Schneider (1930), Banerjee (1934), and James, King & Horrocks (1935): essentially correct atomic coordinates are presented in the last paper. Two independent studies by Fourier methods were performed later: one based on a set of three-dimensional photographic data (Llewellyn, 1947, but see also Abrahams, 1950), the other on two-dimensional data (Abrahams & Robertson, 1947). Several years later Trotter (1961) used Llewellyn's data to refine the structure by ($F_o - F_c$) syntheses. The refinement converged to $R = 0.19$, and led to e.s.d.'s of the atomic positions of 0.02 Å. To our knowledge, no further work on the crystal structure of *p*-dinitrobenzene has been reported. A gas-phase electron diffraction study has been published (Sadova, Popik, Vilkov, Pankrushev & Shlyapochnikov, 1974).

Experimental

Pale-yellow prisms were grown from an acetone solution of the commercial product (Fluka). Oscillation
© 1980 International Union of Crystallography

* Part VII: Colapietro, Domenicano & Portalone (1980).

Table 1. *Crystal data*

p-Dinitrobenzene, C₆H₄N₂O₄, FW 168.11, monoclinic, space group *P*2₁/*n* (systematic absences: *0k0*, *k = 2n + 1*; *h0l*, *h + l = 2n + 1*), *Z* = 2, m.p. = 172–174°C.

	This work		James,	Abrahams &
	Syntex diffractometer ^a	Philips diffractometer ^b	King & Horrocks (1935)	Robertson (1947)
<i>a</i> (Å)	11.137 (2)	11.134	11.05	11.05
<i>b</i> (Å)	3.461 (1)	5.459	5.42	5.47
<i>c</i> (Å)	5.684 (3)	5.681	5.65 ^c	5.67
β (°)	92.22 (4)	92.26	92.3	92.3
<i>V</i> (Å ³)	345.4 (2)	345.0	338.1 ^d	342.4 ^d
<i>D_c</i> (Mg m ⁻³)	1.616	1.618	1.651 ^d	1.630 ^d
<i>D_o</i> (Mg m ⁻³)		1.617 ^e	1.625 ^f	

(*a*) Measured at 293 K with Mo *K* α radiation ($\lambda = 0.71069$ Å). E.s.d.'s are given in parentheses as units in the last digit. (*b*) Measured at 293 K with Cu *K* α radiation ($\lambda = 1.5418$ Å). (*c*) The value of 6.56 Å given in the original paper is not consistent with the given axial ratios (2.038:1:1.043), and is probably a misprint for 5.65 Å. (*d*) Calculated from the given cell parameters. (*e*) Measured at 298 K by flotation in a mixture of carbon tetrachloride and bromoform. (*f*) Lobry de Bruyn (1894).

and Weissenberg photographs confirmed the crystal symmetry reported by James, King & Horrocks (1935) and Abrahams & Robertson (1947). Accurate values for the cell parameters were derived by least squares from the θ values of 15 reflexions, centred on a Syntex *P*2₁ diffractometer (Mo *K* α radiation, θ range 16–21°). An independent measurement was done on a different crystal with Cu *K* α radiation and a Philips PW 1100 diffractometer. The two sets of cell parameters are in excellent agreement, and compare reasonably well with those of previous workers (Table 1).

The intensities were measured at room temperature on the Philips diffractometer in the ω -2 θ scan mode, with graphite-monochromatized Cu *K* α radiation and a crystal 0.4 × 0.3 × 0.5 mm. The scan width was 2.1° in 2 θ , the scan time 10.5 s; the background was measured for 5.25 s at each end of the scan. The θ range explored was 2–65°. A recentring routine was run every 400 reflexions. Three standard reflexions were monitored periodically; their intensities indicated no counter or crystal instability. In all, 1326 reflexions of the symmetry-related octants *hkl* and $\bar{h}\bar{k}\bar{l}$ were scanned. Exclusion of systematically absent reflexions, followed by averaging and merging [internal $R(F_o) = 0.030$], led to a set of 593 independent observations. 564 of these, having $|F_o| \geq 3\sigma(F_o)$, were considered as non-zero and used in subsequent calculations. The intensities were corrected for Lorentz and polarization effects, but not for absorption (μ for Cu *K* α is 1.23 mm⁻¹). A secondary-extinction correction was applied during the final stages of refinement.

Refinement

The positional parameters given by Trotter (1961) for the non-H atoms were used as a starting set ($R = 0.232$). Full-matrix isotropic and then anisotropic least-squares refinement lowered R to 0.145. This value was unusually high; moreover, a difference synthesis failed to show the H atoms. Inspection of the structure factor list revealed that a number of intense reflexions had $|F_c|$ values much greater than the corresponding $|F_o|$'s, indicating that secondary extinction was pronounced in the crystal used. The anisotropic refinement was repeated, omitting the two most intense reflexions from the data set; this led to $R = 0.103$. The H atoms were now easily located on a difference map; their introduction in a structure factor calculation, followed by further refinement of all the atomic parameters, led to $R = 0.055$ (six intense reflexions omitted).

At this stage the intensities were corrected for secondary extinction (Stout & Jensen, 1968). A plot of $\log(I_c/I_o)$ vs I_c was essentially linear for all but the five most intense reflexions, $\bar{1}01$, 111 , 210 , 211 and 310 , which were excluded from the data set. The value of the secondary-extinction coefficient g was 1.66×10^{-4} .

The final refinement was by full-matrix least squares, minimizing $\sum w(|F_o| - k|F_c|)^2$; the number of independent observations per refined parameter was 559/63 = 8.87. Four different weighting schemes were tested (refinements 1 to 4); in all cases the final shifts were $< 0.02\sigma$. Bond distances and angles obtained by the various refinements are compared in Table 2, which also gives the weighting schemes and the values of R and R_w . It is apparent that refinement (4) [$w = 1/(a + b|F_o| + c|F_o|^2)$], although affording a slightly higher R , is superior to refinements (1) to (3) in that it yields a better approximation to the axially symmetrical geometry expected on chemical grounds. A similar observation has been reported for other benzene derivatives (Colapietro, Domenicano & Pela Ceccarini, 1979; Colapietro, Domenicano & Marciantie, 1979; Colapietro, Domenicano & Portalone, 1980); here, however, the effect is quite marked and worth presenting in some detail. Refinement (4) is also that which gives the lowest dispersion for the mean values of the minimized function over ranges of either $|F_o|$ or $\sin \theta/\lambda$.

Another refinement was carried out with a different approach to the secondary-extinction problem (refinement 5). The correction was applied to the F_c 's by refining an empirical isotropic extinction parameter, x , whereby the calculated structure factor becomes $F_c^{\text{corr}} = F_c(1 - x|F_c|^2/\sin \theta)$. The weighting scheme was of the type $w = a/[\sigma^2(F_o) + b|F_o|^2]$, with b chosen so as to minimize the dispersion of the values of the minimized function over ranges of reflexions. The extinction parameter refined to $x = 9.1 \times 10^{-5}$. The molecular geometry obtained by this refinement is hardly different

Table 2. *Effects of different weighting schemes and refinement procedures on the molecular geometry of p-dinitrobenzene*

Bond lengths are given in Å, angles in degrees; e.s.d.'s are 0.002–0.003 Å and 0.1–0.2°, respectively. Atoms are labelled as in Fig. 1.

Refinement Weighting function	(1)	(2)	(3)	(4)	(5)
<i>R</i>	0.0400	0.0394	0.0399	1/(<i>a</i> + <i>b</i> <i>F_o</i>) + <i>c</i> <i>F_o</i> ²)*	<i>a</i> /[<i>σ</i> ² (<i>F_o</i>) + <i>b</i> <i>F_o</i> ²] [†]
<i>R_w</i>	0.0370	0.0396	0.0462	0.0408	0.0414
N–O(1), N–O(2)	1.222, 1.217	1.223, 1.217	1.219, 1.216	1.218, 1.220	1.217, 1.218
O(1)–N–O(2)	124.0	124.1	124.3	124.5	124.4
C(1)–N	1.475	1.474	1.477	1.478	1.478
C(1)–N–O(1), C(1)–N–O(2)	117.4, 118.5	117.5, 118.4	117.5, 118.3	117.6, 117.9	117.6, 118.1
C(1)–C(2), C(1)–C(3)	1.372, 1.379	1.376, 1.380	1.375, 1.377	1.376, 1.377	1.375, 1.376
C(2)–C(3')	1.382	1.383	1.385	1.387	1.386
N–C(1)–C(2), N–C(1)–C(3)	118.7, 118.2	118.6, 118.3	118.5, 118.3	118.2, 118.4	118.3, 118.3
C(1)–C(2)–C(3'), C(1)–C(3)–C(2')	118.8, 118.1	118.7, 118.2	118.5, 118.2	118.4, 118.2	118.5, 118.1
C(2)–C(1)–C(3)	123.1	123.1	123.3	123.4	123.4

* *a* = 0.72, *b* = 1.0, *c* = 0.055.

† *a* = 13.9, *b* = 0.000084.

Table 3. *Final atomic coordinates*

E.s.d.'s from the final full-matrix least-squares cycle are given in parentheses as units in the last digit.

	<i>x</i>	<i>y</i>	<i>z</i>
(a) Non-H atoms (× 10 ³)			
O(1)	12257 (14)	46114 (30)	38013 (27)
O(2)	22066 (13)	47058 (28)	6034 (26)
N	14236 (13)	38916 (26)	18254 (27)
C(1)	6794 (13)	18552 (27)	8674 (25)
C(2)	−3146 (15)	11672 (31)	20710 (28)
C(3)	10152 (14)	7449 (34)	−11810 (27)
(b) H atoms (× 10 ³)*			
H(2)	−52 (2)	194 (4)	344 (4)
H(3)	172 (2)	113 (4)	−197 (4)

* The isotropic thermal parameters of H(2) and H(3) are 3.3 (5) and 3.1 (4) Å², respectively.

from that of refinement (4) (Table 2).

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) (refinements 1 to 4) and of Stewart, Davidson & Simpson (1965) (refinement 5).

Refinements (1) to (4) and other crystallographic calculations were carried out on the Univac 1100/22 computer of the University of Rome, with local programs (Carruthers & Spagna, 1975). Refinement (5) was performed on the CDC 6600 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale, with the *SHELX* 76 system of programs (Sheldrick, 1976).

Results and discussion

The final atomic coordinates from refinement (4) are given in Table 3.* Bond lengths and angles calculated from these parameters are reported in Fig. 1, which also shows the labelling of the atoms; no corrections have been applied for the effects of thermal motion. The equation of the least-squares plane through the six C atoms of the ring and the displacements of all atoms

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34848 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

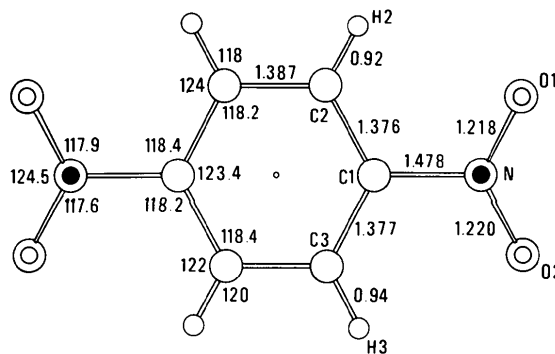


Fig. 1. Bond lengths (Å) and angles (°) in *p*-dinitrobenzene, as obtained from the atomic parameters given in Table 3. E.s.d.'s (calculated from the e.s.d.'s in the atomic parameters) are 0.002 Å for C–C, C–N and N–O bonds, 0.02 Å for C–H bonds, 0.13–0.16° for angles not involving H atoms, and 1.4° for angles involving H atoms.

Table 4. *Deviations from planarity*

Equation of the least-squares plane through the six C atoms of the ring (referred to the crystallographic axes): $5.9991x - 3.5582y + 2.9152z = 0$. The e.s.d.'s in the atomic positions are 0.0014–0.0017 Å for the non-H atoms, 0.02 Å for the H atoms.

Displacements (Å) of atoms from the plane

C(1)	0.000	O(1)	-0.203
C(2)	0.000	O(2)	0.175
C(3)	0.000	H(2)	0.00
N	-0.001	H(3)	-0.06

Table 5. *Torsion angles (°)*

Signs have been given according to the convention of Klyne & Prelog (1960). E.s.d.'s are ca 0.2°.

O(1)–N–C(1)–C(2)	10.7
O(1)–N–C(1)–C(3)	-169.3
O(2)–N–C(1)–C(3)	9.4
O(2)–N–C(1)–C(2)	-170.6

from this plane are given in Table 4. Torsion angles are presented in Table 5. The cell parameters used for geometrical calculations were those measured on the Syntex diffractometer.

The benzene ring

The overall symmetry of the molecule is C_i ($\bar{1}$), as required by space-group symmetry. The symmetry of the C ring, however, is D_{2h} (mmm) within experimental error (Fig. 1 and Table 4). The deviations from D_{6h} ($6/mmm$) symmetry are highly significant, and consist of: (i) a shortening (by 0.010 Å, 5σ) of C(1)–C(2) and C(1)–C(3) with respect to C(2)–C(3'); (ii) an increase from 120° (by 3.4°, 24σ) of C(2)–C(1)–C(3); and (iii) a decrease from 120° (by ca 1.7°, 11σ) of C(1)–C(2)–C(3') and C(1)–C(3)–C(2'). All the effects are consistent with the strong σ -electron-withdrawing character of the NO₂ substituent (Domenicano, Vaciano & Coulson, 1975).

C(2)–C(3'), though longer than the other two C–C bonds, is 0.011 Å shorter than the C–C bond of unsubstituted benzene, 1.398 Å.

The internal angle at the *ipso* atom, $\alpha_{\text{NO}_2} = 123.4$ (1)°, is significantly greater than the average value of 122.1 (1)° obtained by Domenicano, Vaciano & Coulson (1975) from a variety of *para*-substituted derivatives of nitrobenzene. It is, however, in good agreement with the values reported for *p*-nitrobenzoic acid [123.3 (1)° (Colapietro & Domenicano, 1977)], (*Z*)-2-(*p*-nitrobenzoyloxy)-3-phenyl-2-penten-4-one [123.6 (2)° (Stezowski, 1976)], *p*-dimethylamino-benzyl *p*-nitrophenyl sulfone [123.5 (2)° (Tickle,

Hess, Vos & Engberts, 1978)] and *p*-dimethylamino-phenyl *N*-methyl-*N*-(*p*-nitrophenylsulphonylmethyl)-carbamate [123.8 (3)° (Visser, Vos & Engberts, 1978)]. In all these molecules the nitro group is *para* to a strong π acceptor.

Lower values of α_{NO_2} occur in molecules where the nitro group is *para* to a strong π donor, such as *p*-nitroaniline [121.2 (4)° (Trueblood, Goldish & Donohue, 1961) and 121.4 (4)° (Colapietro, Di Rienzo, Domenicano, Portalone & Riva di Sanseverino, 1977)], *p*-nitrophenol [122.3 (4)° in the α form (Coppens & Schmidt, 1965*a*), 121.9 (2)° in the β form (Coppens & Schmidt, 1965*b*)] and the bis(*p*-nitrophenyl)phosphate anion [121.6–122.3° in three different salts (Sax, Pletcher & Gustaffson, 1970; Pletcher, Sax & Yoo, 1972; Yoo, Abola, Wood, Sax & Pletcher, 1975)]. A value of α_{NO_2} as low as 119.1 (5)° has been reported for *S,S*-dimethyl-*N*-(*p*-nitrophenyl)iminosulphurane, a molecule where the general pattern of bond lengths indicates extensive through-conjugation of the substituents (Eliel, Koskimies, McPhail & Swern, 1976).

Intermediate values of α_{NO_2} occur in other molecules where the π properties of the *para* substituent are less extreme, like *p*-nitrostyrene oxide [122.5 (2)° (Williams, Crotti, Macchia & Macchia, 1975)], *p*-nitrobenzamide [122.6 (2)° (Di Rienzo, Domenicano & Foresti Serantoni, 1977)], *syn-p*-nitrobenzaldehyde oxime [122.7 (2)° (Bachechi & Zambonelli, 1973)] and *anti-N*-methyl-*p*-nitrobenzaldehyde oxime [122.7 (3) and 122.9 (3)° (Bachechi & Zambonelli, 1975)].

Although the accuracy of some of the analyses is not very high, there is little doubt that the nature and electronic properties of the substituent have a definite effect on α_{NO_2} in the *para*-substituted derivatives of nitrobenzene, as they have on α_{COOH} in the *para*-substituted derivatives of benzoic acid (Colapietro & Domenicano, 1978; Colapietro, Domenicano & Marcianite, 1978). This finding supports the observation (Domenicano & Vaciano, 1976; Norrestam & Schepfer, 1978) that the effect of a substituent on the internal angles of the benzene ring is not generally limited to α and β , but may extend to γ and δ as well (Fig. 2). The γ and δ angles, although seldom different from 120° by more than 2°, are of importance in the analysis of sub-

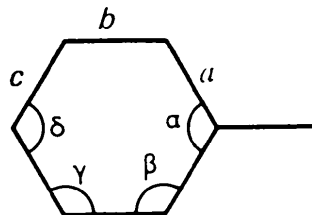


Fig. 2. Labelling of the C–C bonds and C–C–C angles in mono-substituted benzene derivatives. C_{2v} (mm) symmetry has been assumed.

Table 6. *Molecular geometry of nitrobenzene*

Bond lengths are given in Å, angles in degrees. The ring parameters are labelled as in Fig. 2.

	X-ray diffraction ^a	Microwave spectroscopy ^b	Predicted ^c
N—O	1.20, 1.22	1.227	—
C—N	1.49	1.492	—
O—N—O	123.8	124.4	—
<i>a</i>	1.37, 1.36	1.375	—
<i>b</i>	1.39, 1.42	1.403	—
<i>c</i>	1.40, 1.34	1.396	—
α	124.8	125.0	122.9
β	116.5, 116.6	117.1	118.1
γ	121.3, 121.3	120.3	120.3
δ	119.4	120.2	120.4
τ^d	1.9	0	—

(a) Obtained by anisotropic least-squares refinement of the atomic parameters given by Trotter (1959), with the original data set. The refinement converged to $R = 0.116$, with the weighting scheme $w = 1/(a + b|F_o| + c|F_o|^2)$ ($a = 2.0$, $b = 1.0$, $c = 0.02$). The H atoms were fixed at 0.97 Å from the respective C atoms. E.s.d.'s are about 0.015 Å for bond lengths, 1° for angles. (b) Høg (1971). The reported maximum errors are not greater than 0.002 Å for bond lengths, 0.1° for angles. (c) Internal angles of the ring in nitrobenzene, as predicted from the angular parameters of the NO₂ substituent given by Domenicano & Murray-Rust (1979). (d) Angle between the plane of the ring and that of the substituent.

stituent effects, since they reflect the perturbations caused by the substituent in the π -electron system of the ring (Domenicano & Vaciago, 1979; Domenicano & Murray-Rust, 1979). A full set of angular parameters for a variety of substituents has been derived recently by linear regression from accurate literature data for mono- and *para*-di-substituted benzene derivatives, assuming additivity of substituent effects (Domenicano & Murray-Rust, 1979).

In the light of these results, a comparison of the ring geometries of *p*-dinitrobenzene and nitrobenzene would certainly be interesting. A low-temperature (243 K) X-ray diffraction study of this compound was reported by Trotter (1959), but the data set used was rather poor. Refinement of the published atomic parameters by modern techniques with the original data set has afforded the molecular geometry given in Table 6. Detailed comparison with the geometry of *p*-dinitrobenzene obtained here would be inappropriate, because of the high values of the e.s.d.'s. Nevertheless, the effect of the nitro group on the *a* bond lengths and on the α and β angles is seen clearly.

The molecular structure of nitrobenzene has also been determined by microwave spectroscopy. Høg, Nygaard & Sørensen (1971) have shown that the nitro group is coplanar with the ring as in the solid state; Høg (1971) has derived the 'substitution' structure through the analysis of the microwave spectra of all the different monoisotopically substituted species. The

geometry of the heavy-atom skeleton of the molecule is reported in Table 6; it shows the expected pattern of variations for α , α and β .

The 'substitution' method gives very accurate geometrical parameters. In the present case, however, the coordinate of the *ipso* C atom of the ring along the *a* principal axis of the molecule is too small to be determined by the 'substitution' method (<0.30 Å), and has been derived from the first-moment equation (Høg, 1971). This seriously limits the accuracy of the geometrical parameters involving the *ipso* atom.

The last column of Table 6 gives the internal angles of the ring in nitrobenzene, as predicted from the angular parameters of the NO₂ substituent derived by Domenicano & Murray-Rust (1979). The two experimental values of α , 124.8 and 125.0°, are both greater than the predicted value, 122.9°, and also than the value obtained here for *p*-dinitrobenzene, 123.4°. The significance of this surprising discrepancy, however, will remain questionable until more accurate results become available.

The NO₂ substituent

The geometry of the nitro group, including the length of the C—N bond, is close to that observed in *p*-nitrobenzoic acid (Colapietro & Domenicano, 1977). The group is not perfectly coplanar with the C atom of the ring to which it is bonded, C(1), which is 0.032 Å out of the plane through O(1), O(2) and N. Also the N atom is slightly (0.009 Å) out of the plane defined by O(1), O(2) and C(1). The angle between the least-squares plane of the ring and the plane of the substituent is 10.2°, mainly a twist about the C(1)—N bond (Tables 4 and 5).

Table 7. *Molecular geometry of p-dinitrobenzene: comparison of X-ray and electron diffraction results*

Bond lengths are given in Å, angles in degrees.

	X-ray diffraction ^a	Electron diffraction ^b
Molecular symmetry	$C_1(\bar{1})^c$	$D_2(222)^d$
N—O(1), N—O(2)	1.218, 1.220 (2)	1.219 (2)
O(1)—N—O(2)	124.5 (2)	125.7 (3)
C(1)—N	1.478 (2)	1.468 (4)
C(1)—C(2), C(1)—C(3)	1.376, 1.377 (2)	1.387 (3) ^e
C(2)—C(3) ^f	1.387 (2)	
C(2)—C(1)—C(3)	123.4 (1)	121.8 (5)
τ^f	10.2	3 (10)

(a) This work. The figures in parentheses are e.s.d.'s as units in the last digit. (b) Sadova *et al.* (1974). The figures in parentheses are triple e.s.d.'s as units in the last digit. Bond lengths are given as r_a . (c) Imposed by space-group symmetry. (d) Assumed. (e) Mean value. (f) Angle between the plane of the ring and the plane of the substituent.

Comparison with the electron diffraction results

The molecular geometry of *p*-dinitrobenzene obtained here is compared in Table 7 with that obtained by gas-phase electron diffraction (Sadova *et al.*, 1974). The agreement is reasonable, especially if one takes into account the slightly different physical meaning of the quantities that are compared, as well as the possible differences in the effects of thermal motions upon them, apart from any real structural change that may arise from the different state of aggregation. Indeed, two important qualitative features of the ring geometry obtained by X-ray crystallography, namely the increase of α_{NO} , from 120° and the decrease of all the C—C lengths from 1.398 Å, are also present in the ED results. The six C—C bonds of the ring were constrained to equal lengths in the least-squares analysis of the ED intensities, an assumption that is not warranted by our results, and may account for some of the discrepancies. The difference in the angle of twist of the nitro group is of minor importance, due to the large experimental error affecting the ED result, and to the possible effect of packing forces in the crystal.

We thank M. Colapietro and A. Vaciego for stimulating discussions, Mrs C. Marciante for help with the preparation of the drawings, and the Centro di Cristallografia Strutturale del CNR, Pavia, for the collection of the intensities.

References

- ABRAHAMS, S. C. (1950). *Acta Cryst.* **3**, 194–196.
 ABRAHAMS, S. C. & ROBERTSON, J. M. (1947). *Nature (London)*, **160**, 569.
 BACHECHI, F. & ZAMBONELLI, L. (1973). *Acta Cryst.* **B29**, 2598–2600.
 BACHECHI, F. & ZAMBONELLI, L. (1975). *Acta Cryst.* **B31**, 2499–2501.
 BANERJEE, K. (1934). *Philos. Mag.* **18**, 1004–1008.
 CARRUTHERS, J. R. & SPAGNA, R. (1975). *Ital. Crystallogr. Assoc.*, 7th Meet., Bologna, Italy. Abstr. pp. 65–67.
 COLAPIETRO, M., DI RIENZO, F., DOMENICANO, A., PORTALONE, G. & RIVA DI SANSEVERINO, L. (1977). 4th Eur. Crystallogr. Meet., Oxford, England. Abstr. pp. 517–518.
 COLAPIETRO, M. & DOMENICANO, A. (1977). *Acta Cryst.* **B33**, 2240–2243.
 COLAPIETRO, M. & DOMENICANO, A. (1978). *Acta Cryst.* **B34**, 3277–3280.
 COLAPIETRO, M., DOMENICANO, A. & MARCIANTE, C. (1978). *Ital. Crystallogr. Assoc.*, 9th Meet., Sorrento, Italy. Abstr. pp. 75–77.
 COLAPIETRO, M., DOMENICANO, A. & MARCIANTE, C. (1979). *Acta Cryst.* **B35**, 2177–2180.
 COLAPIETRO, M., DOMENICANO, A. & PELA CECCARINI, G. (1979). *Acta Cryst.* **B35**, 890–894.
 COLAPIETRO, M., DOMENICANO, A. & PORTALONE, G. (1980). *Acta Cryst.* **B36**, 354–358.
 COPPENS, P. & SCHMIDT, G. M. J. (1965a). *Acta Cryst.* **18**, 62–67.
 COPPENS, P. & SCHMIDT, G. M. J. (1965b). *Acta Cryst.* **18**, 654–663.
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
 DI RIENZO, F., DOMENICANO, A. & FORESTI SERANTONI, E. (1977). *Acta Cryst.* **B33**, 3854–3858.
 DOMENICANO, A. & MURRAY-RUST, P. (1979). *Tetrahedron Lett.* pp. 2283–2286.
 DOMENICANO, A. & VACIAGO, A. (1976). 3rd Eur. Crystallogr. Meet., Zürich, Switzerland. Abstr. pp. 274–276.
 DOMENICANO, A. & VACIAGO, A. (1979). *Acta Cryst.* **B35**, 1382–1388.
 DOMENICANO, A., VACIAGO, A. & COULSON, C. A. (1975). *Acta Cryst.* **B31**, 221–234.
 ELIEL, E. L., KOSKIMIES, J., MCPHAIL, A. T. & SWERN, D. (1976). *J. Org. Chem.* **41**, 2137–2140.
 HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040–1044.
 HERTEL, E. & SCHNEIDER, K. (1930). *Z. Phys. Chem. Abt. B*, **7**, 188–209.
 HØG, J. H. (1971). Thesis, Univ. of Copenhagen.
 HØG, J. H., NYGAARD, L. & SØRENSEN, G. O. (1971). *J. Mol. Struct.* **7**, 111–121.
 JAMES, R. W., KING, G. & HORROCKS, H. (1935). *Proc. R. Soc. London Ser. A*, **153**, 225–246.
 KLYNE, W. & PRELOG, V. (1960). *Experientia*, **16**, 521–523.
 LLEWELLYN, F. J. (1947). *J. Chem. Soc.* pp. 884–890.
 LOBRY DE BRUYN, C. A. (1894). *Recl Trav. Chim. Pays-Bas*, **13**, 101–147.
 NORRESTAM, R. & SCHEPPER, L. (1978). *Acta Chem. Scand. Ser. B*, **32**, 889–890.
 PLETCHER, J., SAX, M. & YOO, C. S. (1972). *Acta Cryst.* **B28**, 378–387.
 SADOVA, N. I., POPIK, N. I., VILKOV, L. V., PANKRUSHEV, YU. A. & SHLYAPOCHNIKOV, V. A. (1974). *Zh. Strukt. Khim.* **15**, 695–696.
 SAX, M., PLETCHER, J. & GUSTAFFSON, B. (1970). *Acta Cryst.* **B26**, 114–124.
 SHELDRICK, G. M. (1976). *SHELX 76*. Program for crystal structure determination. Univ. of Cambridge, England.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
 STEZOWSKI, J. J. (1976). *Acta Cryst.* **B32**, 2557–2560.
 STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination*, p. 411. London: Macmillan.
 TICKLE, I., HESS, J., VOS, A. & ENGBERTS, J. B. F. N. (1978). *J. Chem. Soc. Perkin Trans. 2*, pp. 460–465.
 TROTTER, J. (1959). *Acta Cryst.* **12**, 884–888.
 TROTTER, J. (1961). *Can. J. Chem.* **39**, 1638–1644.
 TRUEBLOOD, K. N., GOLDISH, E. & DONOHUE, J. (1961). *Acta Cryst.* **14**, 1009–1017.
 VISSER, R. J. J., VOS, A. & ENGBERTS, J. B. F. N. (1978). *J. Chem. Soc. Perkin Trans. 2*, pp. 634–639.
 WILLIAMS, D. J., CROTTI, P., MACCHIA, B. & MACCHIA, F. (1975). *Tetrahedron*, **31**, 993–996.
 YOO, C. S., ABOLA, E., WOOD, M. K., SAX, M. & PLETCHER, J. (1975). *Acta Cryst.* **B31**, 1354–1360.